

Appendix C

2003 WDNR Report – Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) Source Identification

**DRAFT REPORT
POLYCHLORINATED BIPHENYLS
(PCBs) AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)**

**SOURCE IDENTIFICATION
Kinnickinnic River between Becher St. and Kinnickinnic Ave.,
Milwaukee, Wisconsin**

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Wisconsin Department of Natural Resources**

SUMMARY:

The Wisconsin Department of Natural Resources (WDNR) conducted this study to investigate the potential sources that have caused accumulation of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in the sediments of the Kinnickinnic River, Milwaukee, Wisconsin between Becher St. and Kinnickinnic Ave. This source identification project complements efforts by the WDNR, U.S. Army Corps of Engineers, the Port of Milwaukee and the Kinnickinnic River Neighborhood Association to conceptually study the feasibility of different alternatives available to dredge this portion of the Kinnickinnic River for navigational and environmental purposes. Source identification is important for assuring there are no remaining sources of contamination to the study area that will recontaminate the sediment after implementing the dredging plan.

Through review of historical documents and sediment PCB and PAH analyses, we concluded that there are no existing industrial point sources that will contribute substantial amount of PCBs and PAHs into the sediment in the project area. With the exception of a few samples with elevated PAH concentrations in the upper two feet, current analyses showed that the PCBs and PAHs present in the sediment were a result of historical urban growth and development, particularly from the time period of early 1940s to late 1970s. The past possible PCB and PAH sources and transport pathways include coal combustion, transportation of crude and refined petroleum products over the river, discharges from previous industries and vessels, boat engine exhaust, and spills and leakage.

The only concern of potential existing sources is the input from stormwater runoff, combined sewer overflows, and accidental releases that may contain PCBs and PAHs. The Kinnickinnic River is subject to the impact of stormwater runoff and the combined sewer overflows (CSOs). However the concentrations of PCBs and PAHs in current stormwater runoff and CSO streams were relatively low based on the monitoring data collected by the WDNR and the Milwaukee Metropolitan Sewerage District (MMSD). As a typical industrialized urban stream, the Kinnickinnic River is also subject to the impact of accidental spills and leakage. Based on the data available, the majority of the materials from the accidental spills and leakage that occurred in the Kinnickinnic River watershed were petroleum products that may contain PAHs. However PCBs were not present in any of the spill incidents in records.

With the spill law in place, and the continuous implementation of the nonpoint source control plan for the Kinnickinnic River watershed and implementation of community urban stormwater plans, the loading of PAHs and PCBs from nonpoint sources to the Kinnickinnic River will be gradually reduced.

BACKGROUND

I. Site information

The Wisconsin Department of Natural Resources (WDNR), U.S. Army Corps of Engineers (USACE), and US Environmental Protection Agency Great Lakes National Program Office (GLNPO) in conjunction with the Port of Milwaukee and the Kinnickinnic River Neighborhood Association are currently evaluating the feasibility of dredging a stretch of the Kinnickinnic River in Milwaukee, Wisconsin. The dredging will accomplish the purposes of improving navigational condition for commercial and recreational boating and removing a large mass of contaminated sediments.

The project encompasses an area about 2,000 ft long and 200 ft wide, and is located immediately upstream from the federal navigational channel between Becher Street and Kinnickinnic Avenue [Fig. 1]. This stretch of the river is within the Milwaukee Estuary Area of Concern (AOC). The Kinnickinnic River discharges into the Lake Michigan Harbor located approximately 2 miles downstream from the study area. For the convenience of characterization and engineering design purpose, the project area is further divided into three sections as shown in Fig. 1. Starting from Becher St., Section 1 ends at the bend of the river, Section 2 ends before 1st St. and Section 3 is the rest of the area between 1st St. and KK Ave.

Studies conducted from the mid-1980s through 2002 show that sediment in the project area is contaminated with heavy metals, PCBs and PAHs [SEWRPC, 1987, Ni and et. al, 1992a, 1992b; Li and et al. 1995; Altech, 2002], while the primary concerns are of PCB and PAH contamination. Maximum concentrations of 36 ppm PCB and 244 ppm PAH were detected at depth during a 2002 sediment assessment [Altech, 2002]. PAH concentrations of ~1000 ppm were reported earlier [Christensen and et al., 1997].

For the 2002 assessment, seven PCB Aroclors (Aroclor-1016, -1221, -1232, -1242, -1248, -1254, and -1260) were analyzed. The total PCB concentrations were reported as the sum of the Aroclors that were greater than the reporting limits [Altech, 2002]. The total PAH concentrations were the sum of sixteen parent compounds as shown in Table 1. Commonly analyzed C₁-C₄ alkylated PAH homologues series (naphthalene, phenanthrene/anthracene, fluoranthene/pyrene, and chrysene) were tentatively identified and quantified in selected sediment samples. Sum of the estimated concentrations of each compound with the same alkylation level was compared among four groups. For instance, the total concentrations for C₁-Naphthalene were the sum of those compounds with single carbon chain attached to naphthalene on different locations.

II. Characteristic of PCBs and PAHs

PCBs are a group of synthetic chemicals manufactured by adding chlorine to biphenyl. Depending upon the process, a total of 209 compounds or congeners can be created. Mixtures of PCBs were traded under the name of Aroclor in the U.S. As estimated, approximately 40 million pounds of Aroclor were produced in U.S. starting from 1929 until 1977 when the manufacturing was banned [U.S. ATSDR, 2000].

PCBs had been widely used because of their low flammability, low electrical conductivity, high resistance to thermal breakdown and to other chemical agents, and high degree of chemical stability. As summarized in Table 2, PCBs were used in capacitors, transformers, heat transfer units, hydraulic fluids, flame retardant, inks, adhesives, microencapsulation of dyes for carbonless

copying paper, paints, pesticide extenders, plasticizers, polyolefin catalyst carriers, slide-mounting mediums for microscopes, wire insulators, and metal coatings [U.S. ATSDR, 2000].

The physical and chemical attributes that make PCBs useful for industry also cause serious environmental and human health concerns. PCBs are very persistent once released to the environment and can bioaccumulate from the sediments and water column through the food chain from low level organisms to fish [U.S. ATSDR, 2000, Burzynski, 2000]. Chronic low level PCB exposures have been shown to cause liver damage, reproductive abnormalities, immune suppression, neurological and endocrine system disorders in animals and are suspected of causing similar problems in humans [U.S. ATSDR, 2000].

PAHs are a class of chemicals that contain multiple benzene “rings” that are composed of hydrogen and carbon. Variation in the number of rings and their configuration can form a large variety of PAH compounds. Other atoms and carbon chains in various types, different length, and locations can substitute hydrogen atoms on the molecule to either form heteroatomic or alkylated (c-substituted) PAHs. In general those PAH compounds that do not have substitutes are called parent PAHs (C₀-PAHs). For fingerprinting purpose, alkylated or carbon side chain attached PAHs are commonly analyzed in environmental samples. Depending upon alkylation levels, a parent PAH containing one, two or more carbon side chains are referred to as C₁-PAH, C₂-PAH, and so on. There could be a series of c-substituted PAH homologues for different parent PAHs.

PAHs are ubiquitous in the environment [Hites, et. al., 1977]. Some of the compounds are derived from diagenetic sources (i.e. formed naturally) and some are derived from anthropogenic sources (i.e. human activities). PAHs are typically found in or formed by crude oil and its refined products; wood preserving with creosote; manufacturing of electrolytic aluminum using graphitic electrodes; coke production; coal gasification; oil refinery; power generation from fossil fuels; vehicle exhausts; asphalt roads, coal; coal tar; wildfires; agricultural burning, residential wood burning; and incineration of municipal and industrial wastes [US ATSDR, 1995].

With regard to the anthropogenic sources, characteristic PAHs could be found from either petrogenic or pyrogenic origins. Crude oil and its refined products are considered as petrogenic sources that contain higher proportion of lower molecular weight compounds and alkyl PAHs. Incomplete combustion of petroleum, oil, coal and wood can produce those pyrogenic PAHs that are dominated by high molecular weight parent compounds.

Studies show that people exposed by breathing or skin contact for long periods to PAH mixtures can develop cancers. Compounds of benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-c,d]pyrene are either probably or possibly carcinogenic to humans as determined by the International Agency for Research on Cancer (IARC) [US ATSDR, 1995]. The anthropogenic sources are the dominating factor that causes environmental and human health concerns.

SOURCE IDENTIFICATION

I. A review of existing and historical potential point and non-point sources in the vicinity of the project area

An important step in source identification is to investigate both the existing and historical potential point and nonpoint sources that could release significant amount of PCBs and PAHs and recontaminate the sediment in the project area. To the extent possible, a review of various

databases covering the KK River watershed is needed. WDNR reviewed the following databases and related information:

- 1) Wisconsin Pollutant Discharge Elimination System (WPDES) permit program database for point and nonpoint sources
- 2) Contaminated Land Database for unpredictable sources
- 3) Historical Sanborn Fire Insurance Map Collections for historical industries operated in the area
- 4) Milwaukee Estuary nautical charts dated from 1915 through the present time

1. WPDES- Existing point and nonpoint sources

WDNR regulates municipal, industrial, and significant animal waste operations discharging wastewater to surface or groundwater through the Wisconsin Pollutant Discharge Elimination System (WPDES) permit program. According to the WPDES database, within the KK River watershed there is only one industry that holds a specific discharge permit with concerns of heavy metals. There are approximately 45 facilities that hold general permits for discharging their wastewater to the watershed. Almost all of the facilities holding general permits discharge noncontact cooling water only.

Southeast Wisconsin Regional planning Commission (SEWRPC) provided a detailed list of the businesses currently located in the vicinity of the study area. Table 3 summarizes the type of those businesses and Fig. 2 shows their locations corresponding to the index number listed in the table. Specifically between Becher St. and KK Ave., the riparian owners include marinas, marine services, business services, and auto parts salvage yard. At this point none of these businesses directly discharge wastewater to the KK River.

The potential regulated sources of concern are the input from non-point sources. Further investigation of nonpoint sources that under regulation was warranted particularly that PAH concentrations in surficial sediment (0-2ft) around 1st St. increased compared to that in the underlying sediment interval, an indication of potential recent PAH deposition in the area.

With that regard staff from Southeast Region of WDNR paid several visits to an auto salvage yard for possible sign of discharge. As a result, it was concluded that the auto salvage yard appeared to be mostly covered with clean gravel [Bosch, 2003]. There was no obvious overland drainage pathway although the general drainage direction was toward the river. Additionally, no significant erosion from the site was present during visits.

Another industry that holds WDNR's urban storm water discharge permit is an iron & steel foundry facility that is located on S. 4th St. The company is required to submit stormwater runoff monitoring data to WDNR under WPDES. Biological oxygen demand (BOD), total suspended solids (TSS), and Oil&Grease are the monitoring parameters. Although PCBs and PAHs are not the parameters of interest, the concentration of Oil&Grease may serve as an indicator for organic contaminants. According to the results collected from two sampling events, the concentrations of Oil& Grease ranged from less than 2 mg/l to 5 mg/l, which did not raise a serious concern compared to Wisconsin statewide database.

As a summary, the regulated point and nonpoint dischargers will not be of concern as significant sources to recontaminate the sediment with PCB and PAHs at this time.

2. Contaminated Land Database -Unpredictable sources

As opposed to the regulated sources, there may be unpredictable potential existing sources. KK River, a typical industrial urban stream, is subject to the impact of stormwater runoff, CSOs, emission from boat engine exhaust, and incidental spills and leakage. If PCBs and PAHs are present high in those streams it could be a serious concern.

Existing data collected from studies and routine monitoring in concern of the unpredictable potential sources were reviewed for the levels of PCB and PAHs. Based on the monitoring data collected by the MMSD and WDNR [1994] PCBs and PAHs would be in a low concentration range if detected in the stormwater runoff and CSO streams since 1980s. That means the stormwater runoff and CSO are not to be expected to contribute significant amount of PCB and PAHs to the project area at present time.

With respect to the spills and leakage, the Contaminated Land Databases maintained by the Bureau for Remediation and Redevelopment Tracking System (BRRTS) of WDNR were reviewed. From 1980s there have been several cases of spills occurred in the vicinity of the project area. Most of the reported accidents involved grease & oil, unleaded fuels, and diesel fuels. For instance, a 1993 accident over the KK River, perhaps downstream of KK Ave., resulted in a barge sank and about 20 gallons of diesel fuel released. The release of petroleum related products might cause high PAH concentrations in sediment.

The underground storage tanks (LUST) could be a concern too. There were several leaking underground storage tank sites located on the properties in the project area. However, according to WDNR's record all of these sites have been studied and correction actions were taken place. They were closed in 2001 with a GIS registration regarding the groundwater issues for two remaining sites.

Exhaust from boat engine could be a direct source of PAHs to water column and hence the sediment. As Fig. 3 shows that the number of boats registered in Wisconsin has increased steadily since 1960. However, there are no particular data readily available for review with respect to PAH emission. The significance of the recreational and commercial boating on the contribution to PAHs in the sediments is unknown at present time. With the implementation of the federal rule on control of emissions from spark-ignition marine vessels and highway motorcycles as proposed in 2002 the emission of particulate and hence PAHs will be gradually reduced [Federal Register, 2002].

Because PCBs and PAHs continue to exist in many industrial, commercial, and residential contexts, their release undoubtedly could occur in future. However, with the spill law enforcement and LUST program and efforts in reducing the nonpoint sources by local communities along with the continuous implementation of nonpoint source control plan for the KK River watershed [WDNR, 1994] the release of PCBs and PAHs from those unpredictable sources will be reduced. It is believed that the overall water quality in the runoff stream will be further improved.

3. Historical Sanborn Fire Insurance Map Collections

To identify potential historical PCB and PAH sources, Sanborn Fire Insurance Map Collections at the Wisconsin State Historical Society were reviewed. The detailed drawings of the property locations showed that between 1900s and 1970s a number of various industries and businesses operated in the project area that was in parallel to industrialization and urban growth nationwide. About eight major companies resided between Lincoln Ave. and KK Ave. in 1930s and then the

number of businesses increased to more than twenty in 1950s. The approximate locations of those businesses are shown in Fig. 4 with the index numbers that are described in Table 4.

As it can be seen from Tables 3 and 4, the type of businesses have changed significantly since 1930s to present. In 1930s and 1950s industries, including steel works, shoe manufacturing, tannery factory, wood works, brass foundry, iron works, coal wood & lumber yard, fuel company, leather company, ice making, and manufacturing of commercial refrigeration parts, predominately occupied the area. At present time, majority of the businesses is related to marina services.

From the reviewing of the type of industries historically operated in the project area it is suspected that these industries might have handled wastes containing PCBs and PAHs. But at present time it is difficult to identify which company was responsible for the problem due to the complexity of the types of businesses and their evolving processes. In addition, to make the case even more complicated is that almost all of these historical industries no longer exist in the area.

4. Milwaukee Estuary nautical charts

In addition to the Sanborn Fire Insurance Map Collections, the historical nautical charts indirectly recorded information on the urbanization in the project area because Milwaukee Harbor has a long history as one of the industrially developed harbor [Board of Harbor Commissioners, 1965]. Subsequently, those nautical charts also recorded the changes of the water column depth through the years and could be used to estimate sedimentation rates.

A series of Milwaukee Estuary nautical charts dated from 1915 to 1997 (Figures 5-11) were obtained. Those nautical charts clearly showed that historically the river was designed to accommodate commercial navigational need. Water depth in the river channel has gone substantial changes over the years. The stretch of the river between Lincoln Ave. and First St. was dredged down to as deep as 21ft (1936 chart, Fig. 6) and three drawing bridges were constructed to accommodate large boats. However, by 1940s, routine dredging stopped and accumulation of sediment resulted in a shallow condition in the stretch of the river. As shown on the charts the maximum water depth decreased gradually from 21ft (1936 chart) to 8ft (1978 chart). Table 5 summarizes the temporal changes of water column depth relative to the datum used and the elevation of water-sediment interface relative to the International Great Lakes Datum 1985 (IGLD85) at 577.5ft.

An attempt was made to use the temporal record of water column depth and hence the elevation of sediment-water interface to estimate sedimentation rates at the locations where sediment cores KK-0202 and KK-0209 were collected in 2002 assessment. These two cores were chosen for analyses because substantial amount of sediment has accumulated at these two locations and the concentrations of PCBs and PAHs were relatively high.

The first step in the sedimentation rate estimation was to estimate how many feet of sediments have accumulated since 1936 when the deepest river channel was recorded based on the nautical charts. Clearly, the difference of the sediment-water interface elevation between year 2002 [Coleman Engineering, 2002] and 1936 (Fig. 6) would be the sediment thickness that accumulated during the time period. It should be noted that discussion of elevation thereafter is referenced to IGLD85 datum. For instance, the elevation of the sediment-water interface at location KK-0202 in 2002 was at 574 ft (4 ft of water), while it was at 557ft (21 ft of water) in 1936 (Fig. 6); therefore, the difference of approximately 17 ft would be the sediments accumulated between 1936 and 2002. As a result, sediment at the depth of 16-18 ft at core KK-

0202 was assigned with a date of 1936 approximately. Using the same assumption, since the 1944 nautical chart showed that water column depth reduced from 21 ft to 18ft, the segment interval of 14-16ft was then assigned to 1944. For the rest of segment intervals, if no direct link of a sediment interval to a nautical chart date could be determined, the temporal history of the sediment interval was estimated based on linear interpretation of the sedimentation rates between two consecutive chart dates.

Table 6 summarizes the estimated sedimentation rates for the analyzed areas. It is not surprising to see that the rates vary in a range of 0 - 0.67 ft/yr (0 - ~20cm/yr) with a fast sedimentation recorded in the time period of 1940s through 1970s.

Coinciding with the fast sedimentation rates, PCB and PAH concentrations also reached a maximum in about 1960s as shown in Fig. 12. Prior to early 1930s PCBs were either not available or used little, the concentrations in sediment were much lower. Steady increase was shown since then until 1960s. After 1960s PCB concentrations decreased again maybe due to the ban of PCB manufacturing and implementation of environmental control policies as well as the change of the nature of the industries and businesses in the area. The increase of PCBs in the top 2-ft sediment at location KK0202 may be resulted from resuspension and redistribution of PCBs from other places to this depositional area. Also the difference is somewhat within the analytical variation.

While PCB profiles showed a clear maximum in the cores, PAHs profiles changed less consistently as shown in Fig. 12. Although PAH concentrations reached a maximum in 1960s, several less significant peaks also exist. The variation may be contributed to more complicated origination of PAHs. The use of different types of energy, the change of vehicle exhaust systems in addition to environmental regulations, and the change of type of businesses in the area can have compounded effects in the total PAH concentrations. Such variation along with a peak concentration in 1960s observed in the project area was similar to that observed in Lake Michigan sediment [Christensen and Zhang, 1993], the Pettaquamscutt River, South Kingston, Rhode Island [Lima et. al., 2003], and Grand Traverse Bay, Lake Michigan [Schneider et. al., 2001].

Other historical records also support the trend that the PCBs and PAHs reached the maximum level between 1940s and 1960s due to industrialization and urban development. Board of Harbor Commissioners [1965] reported that between 1946 and 1959 the total seaway trade at the Port of Milwaukee increased by approximately 80 times, while between 1959 and 1965 it quadrupled, a reflection of the urban growth and development in the time period in the Milwaukee Estuary. In addition, profiles of carbon particles from the KK River [Karls and Christensen 1998] also revealed that the percent of carbons peaked around 1940s in the sediment.

There were several exceptions of the total PAH profiles at locations around 1st St where Cores KK0209, KK0211, and KK0212 were taken. The concentrations of PAHs in the top 2-ft sediment interval were higher than that in the overlying layer. PAH profile in KK-0209 as shown in Fig. 12 is typical for those cores although the concentrations may differ. The increase trend in the top layer may indicate a recent input of PAHs to the sediment.

However, it should be pointed out that field record indicated that even within the top 2-ft sediment interval the physical characteristics of the upper 6-inch sediment were different from the lower 6-inch sediment at KK0209 [Coleman Engineering, 2002]. The upper 6-inch sediment was composed mainly of loose gray fine to medium sand materials while the lower 6-inch sediment was composed of soft, black elastic silt. Based on the estimated sedimentation rate of 0.08ft/yr between 1978 and 2002 at this location, it is suggested that the black silt materials were deposited

between 1978 and 1996, an indication that the increase of PAHs in the top 2-ft sediment was not a result of most current discharge.

On the other hand, multiple sources ranging from the increased traffic since 1970s as indicated in studies by van Metre et. al. [2000] to incidental spills and leakage could contribute to the increase of PAHs. But because the relative abundance of parent PAHs in this sediment interval was similar to that in the deeper sediment as will be discussed later, it is hard to determine which specific source has caused the recent increase.

As a summary, the results from reviewing various current and historical point and nonpoint sources and the related information supported the assumption that the PCBs and PAHs in the sediment of the project area were primarily associated with industrial development and urbanization historically.

II. Analyses of local sediment background level of PCB and PAHs

In addition to the point and non-point sources, the sediment existing in the upper KK River (upstream from Becher St.) could be potential sources if it is highly contaminated. Because most of the river channel upstream from the Chase Ave. has been concrete channelized, the sediment loading to the KK River will most likely deposit downstream of the Chase Ave. That makes the portion of the stream between Chase and Becher St. (Fig. 1) becoming the first choice as the local background site.

As part of the 2002 sampling protocol, two grab samples (KK-02US1 and KK-02US2) were collected from the background site [Altech, 2002]. On Feb. 27, 2003 WDNR collected nine additional samples, KKUS03-01 through KKUS03-09, as shown in Fig. 1. A large sand bar existed right at downstream from Chase Ave. where the MMSD's flushing station is located. As a result, a composite surface sediment sample (KKUS03-08) at three relative locations from this sand bar was collected.

The samples were collected in accordance with WDNR's sampling procedures. Grab samples were collected using a petite ponar through ice with the aid of a power auger to break the ice. A global positioning system (GPS) unit was used to determine the sample locations. Where it was not possible to obtain sediment materials by using the ponar, a spoon was used. Upon retrieval, sediments were mixed in a stainless steel mixing bowl and subsampled into a 500ml Mason Jar and stored in a cooler on ice under the air temperature of 0°C. By the end of the day, samples were transported from Milwaukee to Madison and stored in a refrigerator. On Feb. 28, the samples were delivered to the Wisconsin State Laboratory of Hygiene, Madison, Wisconsin for analyses of PCBs, PAHs, and particle size. PCBs were analyzed in six samples while PAHs in all the samples. The same QA/QC processes as described in the 2002 [USACE, 2002] sampling protocol were followed for the 2003-sampling event. Samples KKUS0301 and KKUS0302 served as field duplicates.

It was observed in the field that little soft sediment has accumulated in the background site, particularly from Chase Ave. to Lincoln Ave. All of the samples contained high fraction of sand that ranged from 88 to 98% [Table 6].

In general, PCB and PAH concentrations in background sediment were lower compared to that in the surficial sediment from the project area as shown in Fig. 13. The concentrations ranged from 21 to 347 ppm with an average of 67 ppm for the total PAHs and 0.1 to 2.2 ppm with an average of 0.8 ppm for the total PCBs. The sample (KKUS03-06) with a maximum PAH concentration of

347ppm contained materials of a distinctive odor that was not present in other samples, which indicated that the sediment was contaminated with an isolated source. Although the PAH concentration was high at this particular location, it is believed that the impact of these materials from the KKUS03-06 to the project area would be small compared to the overall PAH concentrations in the background site. Therefore, it is concluded that at present time the upstream sediment is not a significant source of PCBs and PAHs to the project area.

III. Analyses of distribution patterns of PCBs and PAHs

A common approach to identify sources of PCBs and PAHs in the environmental samples is “fingerprinting” by comparing the composition of PCBs and PAHs in environmental samples to that in potential sources. This approach could be very useful in some cases, but it often proves increasingly difficult for sediment samples. After PCBs and PAHs released to an aquatic system, the effect of continuous dynamic hydrological, chemical, physical, and biological processes can alter the original composition greatly, not to mention that the original sources are complex. This profound alternation by the nature is also superimposed by human activities such as dredging. Nevertheless, the fingerprinting of PCBs and PAHs may still contain some information regarding the sources. The following discussion will describe the effort in identifying the sources based on the variation of PCB and PAH compositions in sediment and related studies for the project area. Some of the information will be useful to prove that the highest concentrations of PCBs and PAHs detected in the sediment were related to historical sources.

PCBs

With respect to specific types of sources that caused PCB contamination in the sediment, the Aroclor patterns detected in the sediment were analyzed. In general there were two characteristics of PCB distributions in the sediment. First, consistently, Aroclor 1242 was the dominating type in almost all of the surficial sediment samples with an exception that Aroclor 1248 dominated in samples KK-0201-0002 and KK-0206-0002. Also Aroclor 1242 dominated in the upstream background site. Secondly, in the sediment buried deeper than 2-ft different types of Aroclors dominated in different sections of the project area. As Fig. 14^a shows, in Section 1 (where cores 1 to 4 were collected), Aroclor 1248 and 1254 were the most abundant types; while in Section 2 (where cores 5 to 7 were collected) depending upon depth of the sediment from the surface, either Aroclor 1242 or 1248 was abundant. Further downstream in Section 3 (where cores 8 to 14 were collected) Aroclor 1242 was the most abundant type with a few exceptions. For instance, Aroclor 1248 dominated in the deeper sediment, primarily in the segment interval of 8-10ft, corresponding to approximately in late 1960s according to KK-0209 sediment dating (Fig. 12).

The consistency of Aroclor 1242 being the most abundant in the surficial sediments (top 2ft) may be influenced by its predominant production in late 1970s in the U. S. [U.S. ATSDR]. Also it may reflect the current condition in the background. But the shift of the abundant types of Aroclors in the sediment buried deeper definitely implied to the different origins of PCBs. Due

^a Fig. 14 shows the Aroclors detected in sediment samples collected in 2002 and 2003. Quantification of Aroclors could be complicated due to interference. To better assess the potential PCB patterns, the Aroclors that were detected at or below the reporting limit are also plotted in the figures. Particularly, because the reporting limit for Aroclor 1254 was relatively high, it is necessary to show the potential concentrations.

to the wide use and spread of Aroclors 1248 and 1242 this analysis was not able to differentiate one particular source from the others.

PAHs

For the purpose of comparison, parent PAH compounds were arbitrarily divided into eight groups based on the number of carbons each compound contains. The eight groups are C10, C12, C13, C14, C16, C18, C20, and C22 as show in Table 2. To further simplify the analyses, the sum of the concentrations of each group was normalized to the sum of the C16 compounds, specifically, Fluoranthene and Pyrene. The reason to normalize the concentrations to the C16 compounds was that these two compounds were most abundant in all the sediment samples collected from the project area.

Comparison of the normalized PAH patterns were made in the samples collected from the Manufactured Gas plant site and from this project. Also the characteristics of PAH distributions in nonpoint sources and in the sediment from the project were compared. Finally the tentative analyses of PAH homologues series are presented.

The following analyses were based on general understand that individual PAH parent compounds could differ from one sediment sample to another due to different sources, the hydraulic conditions the sediment was exposed to, and their physical, chemical, and biological characteristics. Weathering can selectively remove the lighter and more water-soluble hydrocarbons, unbranched and less alkyl substituted PAH. In general, if lower molecular weight PAHs are dominant, most likely the sediment is contaminated by crude oil and its related products. In contrast if higher molecular weight PAHs are dominant, the sediment is possibly contaminated with combustion sources, coal tar and distillates, and heavy residuals in the array of petroleum products.

In comparison to PAHs identified at a manufactured gas plant (MGP) site

Milwaukee Solvay Coke Gas plant (MSCG) operated at a location downstream from the KK Ave. until the early 1980s. It may be assumed that PAHs present in the upland could be the potential sources to the sediment of the KK River immediate off the previous MSCG plant location. It is then necessary to compare the composition of PAHs in the project area to that at the MSCG site to determine if the MSCG plant was a potential significant source.

Site assessment has been conducted by USEPA on the land as well as in the sediment at the MSCG site [Tetra Tech, 2002]. Normalized PAH concentrations in tar, heavy oil, and contaminated soil and materials from excavated pits are presented in Fig. 15. As can be seen from the plots the distribution of PAH compounds in different sample matrices varied significantly.

In both the tar and heavy oil samples, low molecular weight compounds were most abundant. Concentrations of C18 through C22 compounds were relatively less but the ratios to C16 compounds were either close to or greater than 1. This distribution pattern changed in the soil samples with much higher variation in space. Compounds lighter than C14 were present at a less abundant level, so was the higher molecular weight compounds. Possible mixing of PAHs from various origins as well as weathering or degradation in environment could contribute the change of the composition in the sample matrices.

As to the sediment samples collected from the KK River off the MSCG site, the PAH composition not only varied significantly from what was observed in the upland samples but also varied in space. The abundance of lower molecular weight compounds decreased significantly except for samples from Station 9 (Fig. 16). At this particular place, naphthalene was the most abundant PAH, which might be resulted from recent release of coal tar, spills, or leakage of petroleum products.

The significant decrease of lower molecular weight PAHs in sediment samples compared to that in the upland samples might be contributed by two factors. One is that the portion of the river under MSCG assessment is within the federal navigation channel, majority of the PAHs historically released from the MSCG facility may no longer exist because the channel has been routinely dredged. The second factor affecting the composition is the loss of lower molecular weight compounds due to degradation and higher water solubility.

As part of the MSCG site assessment, sediment samples were also collected upstream from Kinnickinnic Ave. Station 12 was close to where core KK-0202 was located from this project. Another grab sample (Station 11) was collected from further upstream between Chase and Lincoln Ave. Comparison of PAH distribution patterns at these two locations (Fig. 16) with that at the rest of MSCG locations shows that in general C12, C14, C18, and C22 compounds were much less abundant.

Also the distribution pattern at Station 11 and 12 was consistent with what have been observed in the samples collected from our project area in 2002 (Fig. 17). Most significantly, naphthalene was detected at a level less than the reporting limits in samples from Station 11 and 12 of MSCG assessment, which was consistently the case in all the 2002 samples. But naphthalene was the most abundant in tar and heavy oil samples and also it was detected in most of the upland soil and sediment samples collected from MSCG site.

Therefore, it is concluded that MSCG site is not the major contributor to the PAH problem between Becher St. and KK Ave. This conclusion is also supported by the compound-specific analyses documented in the MSCG site assessment report. According to the report, samples collected from upstream of Kinnickinnic Ave. did not contain 1,2,3-trimethyl-4-propenyl-naphthalene, a compound that is associated with manufactured gas plant sites [Tetra Tech, 2002].

With regard to the distribution of PAHs in sediment at this project area, fluoranthene and pyrene dominated in all of the sediment samples with a fairly consistent pattern in all the samples as shown in Fig. 17. That means the PAHs were most likely originated from combustion and little degradation has occurred to the high molecular weight compounds.

In comparison with PAHs in highway dust and stormwater runoff

PAHs in stormwater runoff and CSOs could originate from highway dust, vehicle exhaust, spills of oils and petroleum products, and atmospheric deposition. Highway dust has been identified as the most significant nonpoint source contributing PAHs into the Milwaukee Harbor Estuary [Singh *et al.*, 1993; Christensen *et al.* 1997, Li *et al.* 1998]. To evaluate the significance of the various nonpoint sources input of PAHs into the sediment, the distribution patterns of PAHs in highway dust, engine exhaust, and runoff samples were reviewed. Figure 18 shows the composition of the average PAHs from highway dust and gas engine exhaust [Singh *et al.*, 1993] and in runoff samples [USGS, 1999; Hewitt and Rashed, 1992].

Similar to PAH composition in sediment samples, fluoranthene and pyrene were the most abundant PAH compounds in the nonpoint source samples as presented in Fig. 18. The distribution pattern in the nonpoint sources did not differ significantly from that in the sediment samples. However, as shown in Fig. 17 and 18, the ratio of C22 compounds to C16 compounds was around 0.2 in highway dust samples and engine exhaust while it ranged from 0.2 to 0.4 with a few exceptions in the sediment samples.

The runoff water samples collected by USGS from the maintenance garage and parking facility in Milwaukee showed high similarity in PAH composition to the sediment samples, which implies that stormwater runoff could be one of the major sources to PAH contamination in sediment. However, the significance of impact in the overall total PAHs in sediment compared to the direct historical industrial sources at the project area is unknown at this time. In addition, it will be difficult to actually identify the weight of contribution from each source to PAHs in the sediments.

PAHs homologues series

Results from the tentative identification and quantification of alkyl (c-substituted) PAHs or homologues series in selected 2002 sediment samples are displayed in Fig. 19. The purpose of analyzing those homologues series is to make an attempt to differentiate petrogenic versus pyrogenic sources. According to studies, petroleum and its products contain higher proportion of c-substituted PAHs (petrogenic origin) while combustion of coal and petroleum produces higher proportion of parent PAHs (pyrogenic origin). Visually the concentrations of homologues groups could be plotted in a sequence of C₀-, C₁-, C₂-, C₃-, and C₄- PAHs, and subsequently the shapes of the distribution pattern, bell-shaped or skewed, can be used for identifying the origin of PAHs [Battelle].

Little interpretation can be made to the results from the tentative analyses. C₁-PAHs were the most abundant PAHs in all groups. This could indicate that little degradation has occurred for parent PAHs, but it could also indicate that petroleum related products could be one of the sources while the low molecular weight compounds almost disappeared due to weathering and its high solubility in water. In addition, because the quantification of c-substituted compounds was tentative, the results could contain higher analytical uncertainties for any detailed analyses.

IV. Conclusion

It is concluded that based on the analyses conducted at this point that higher contamination of the PCBs and PAHs in the project area sediments were mainly caused by historical discharges, spills, and other input associated with industrial activities and urban development. Due to the changes in type of businesses historically and the complexity of the sources no individual industry could be identified to be responsible for the problem. The reason for the increase of PAHs in surficial sediment in Section 3 may be related to accidental release from spill of heavy oils or other wastes, emission from the increased recreational and commercial boating, and resuspension and redistribution of PAHs might be the possible causes.

The attempt to use the composition of PCBs and PAHs in sediment for source identification may be useful but not successful in further differentiation of specific sources. PCBs have been widely used prior to the ban in manufacturing in late 1970s. The origin of the PCBs in sediment can not be easily defined although Aroclor 1248 and 1242 were the dominating PCBs. Source identification of PAHs based on their composition was even more difficult because the origin of PAHs is much more complicated and also environmental degradation could alter their

composition. Comparison of parent and alkylated PAH compounds did not identify a particular source. It is speculated that a combination of industrial discharges; accidental spills of heavy oils and fuels; emission of combustion from industries; commercial and recreational boating; and stormwater runoff was the cause for the high PAHs in the sediment. It has to be emphasized here that all of these possible significant sources were historical sources. There are no existing sources that will continue to contribute significant contaminants, particularly PCBs to the project area.

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Table 1. List of parent and methyl substituted PAH compounds

| Compounds analysed in all samples | | | Tentatively identified compounds | |
|-----------------------------------|---------|----------------|----------------------------------|-----------|
| Chemical | Abbrev. | No. of Carbons | Chemical | Abbrev. |
| Naphthalene | Nap | c12 | C1-Naphthalene | C1-Nap |
| Acenaphthylene | AcNP | c12 | C2-Naphthalene | C2-Nap |
| Acenaphthene | AcN | c12 | C3-Naphthalene | C3-Nap |
| Fluorene | Fl | c13 | C4-Naphthalene | C4-Nap |
| Phenanthrene | PhA | c14 | C1-Phenanthrene/Anthracene | C1-PhA/AN |
| Anthracene | AN | c14 | C2-Phenanthrene/Anthracene | C2-PhA/AN |
| Pyrene | Py | c16 | C3-Phenanthrene/Anthracene | C3-PhA/AN |
| Fluoranthene | FIA | c16 | C4-Phenanthrene/Anthracene | C4-PhA/AN |
| Benzo(a)anthracene | BaA | c18 | C1-Fluoranthene/Pyrene | C1-FIA/Py |
| Chrysene | Chy | c18 | C2-Fluoranthene/Pyrene | C2-FIA/Py |
| Benzo(b)fluoranthene | BbFIA | c20 | C3-Fluoranthene/Pyrene | C3-FIA/Py |
| Benzo(k)fluoranthene | BkFIA | c20 | C1-Chrysene | C1-Chy |
| Benzo(a)pyrene | BaP | c20 | C2-Chrysene | C2-Chy |
| Indeno(1,2,3-cd)pyrene | IP | c22 | C3-Chrysene | C3-Chy |
| Dibenzo(a,h)anthracene | dBahA | c22 | C4-Chrysene | C4-Chy |
| Benzo(g,h,i)perylene | BghiP | c22 | | |

Table 2. Summary of former end uses of various Aroclors (ATSDR, 2000)

| | | Aroclor | | | | | | | | |
|------------------------|---------------------------------|---------|------|------|------|------|------|------|------|------|
| End Use | | 1016 | 1221 | 1232 | 1242 | 1248 | 1254 | 1260 | 1262 | 1268 |
| | | | | | | | | | | |
| Capacitors | | x | x | | | | x | | | |
| Transformers | | | | | x | | x | x | | |
| | Heat transfer | | | | x | | | | | |
| Hydraulics/lubricants: | | | | | | | | | | |
| | Hydraulic fluids | | | x | x | x | x | x | | |
| | Vacuum pumps | | | | | x | x | | | |
| | Gas-transmission turbines | | x | | x | | | | | |
| Plasticizers: | | | | | | | | | | |
| | Rubbers | | x | x | x | x | x | | | x |
| | Synthetic resins | | | | | x | x | x | x | x |
| | Carbonless paper | | | | x | | | | | |
| Miscellaneous: | | | | | | | | | | |
| | Adhesives | x | x | x | x | x | | | | |
| | Wax extenders | | | | x | | x | | | x |
| | Dedusting agents | | | | | | x | x | | |
| | Inks | | | | | | x | | | |
| | Cutting oils | | | | | | x | | | |
| | Pesticide extenders | | | | | | x | | | |
| | Sealants and caulking compounds | | | | | | x | | | |

**Table. 3 Type of Businesses Located Along the Kinnickinnic River Within the Study Area
(SEWRPC, 2000)**

| No. on the map | Type of Business | No. on the map | Type of Business |
|----------------|-------------------------------|----------------|-------------------------------|
| 1 | Wrecking & Demolition | 20 | Fabricated Metals |
| 2 | Boat Dealer | 21 | Publishing |
| 3 | Furniture Manufacturer | 22 | Electronic Components |
| 4 | Restaurant | 23 | Fruits & Vegetables |
| 5 | Cement | 24 | Prepared Meat Products |
| 6 | Used Auto Parts | 25 | Police |
| 7 | Commercial Fishing | 26 | Photo Laboratory |
| 7 | Metal Heat Treating | 27 | School |
| 8 | Boat Dealer | 28 | Delivery Service |
| 8 | Canvas | 29 | Trucking |
| 8 | Gas Sales | 30 | Bar |
| 8 | Marina | 31 | Auto Repair Shop |
| 9 | Iron & Steel Foundry | 32 | Bar |
| 10 | Accounting | 33 | Bar |
| 10 | Business Services | 34 | Bar |
| 10 | Computer Programming | 35 | Bar |
| 10 | Computer Programming | 36 | Bar |
| 10 | Interior Design | 37 | Automatic Merchandising |
| 10 | Investment Services | 37 | Commercial Equipment |
| 10 | Janitorial | 37 | Wood Office Fixtures |
| 11 | Marina | 38 | Commercial Printing |
| 12 | Business Services | 39 | Arrangement of Transportation |
| 12 | Commercial Printing | 39 | Auto Repair Shop |
| 12 | Flooring | 39 | Industrial Machinery |
| 12 | Industrial Machinery | 39 | Mosaic Work |
| 12 | Industrial Machinery | 39 | Plating & Polishing |
| 13 | Used Auto Parts | 40 | Armored Car Services |
| 14 | Warehousing & Storage | 40 | Business Services |
| 15 | Special Trade Contractors | 40 | Commercial Photograph |
| 16 | Industrial | 40 | Motor Vehicle Supplies |
| 17 | Marina | 40 | Outdoor Advertising |
| 18 | Masonry | 41 | Fruits & Vegetables |
| 19 | Arrangement of Transportation | 42 | Department Store |
| 19 | Trucking | 42 | Restaurant |

Table 4. List of Businesses (~1930s and ~1950s)

| Around 1930s | | Around 1950s | |
|---------------------|-------------------------------|---------------------|--------------------------------------|
| Index No. | Company Name | Index No. | Company Name |
| O1 | Fred Reuping Leather Co. | H1 | Milwaukee Blast Furnace |
| O2 | Clear Ice Co. | H2 | Shum Co. (Chemical) |
| O3 | Sands Lumber Co. | H3 | Crucible Brass Foundry |
| O4 | Maynard Steel Casting Co. | H4 | W.C. Luebke Coal Co. |
| O5 | Milwaukee Stove Works | H5 | A. F. Wagner Iron Works |
| O6 | Vulcan Iron & Steel Works | H6 | Pioneer Foundry Corp. |
| O7 | Harsh Smith Edmunds Shoes Co. | H7 | Milwaukee Shoe Co. |
| O8 | Milwaukee Brewing Co. | H8 | Wisconsin Leather Co. |
| | | H9 | AELCO Brass Foundry Inc. |
| | | H10 | The Great Atlantic & Pacific Tea Co. |
| | | H11 | Fire Department |
| | | H12 | Edward E. Gillen Co. |
| | | H13 | J. Lesczynski Coal & Woodyard |
| | | H14 | Milwaukee Western Fuel Co. |
| | | H15 | The Filer & Stonwell Co. |
| | | H16 | The Vilter MFG Co. |
| | | H17 | M. Sanderson Co. |
| | | H18 | Milwaukee Preserve & Flavor Co. |
| | | H19 | Dyeing & Bleach Plant |
| | | H20 | Wood Works |
| | | H21 | Brick yard |

Table 5 Change of water depth at selected locations*

| | Water Depth (ft) | | | | | | |
|--|---|-------|-------|-------|-------|-------|-------|
| Year | 1915 | 1936 | 1944 | 1951 | 1960 | 1978 | 1997 |
| Chart reference datum** | 578.5 | 578.5 | 578.5 | 578.5 | 578.5 | 576.8 | 577.5 |
| Locations: | | | | | | | |
| at half way between Chase and Linclon Ave., at Lat. 43°00' | 3 | 11 | 11 | 11 | 3 | 3 | 3 |
| at Lincoln Ave. | 10 | 18 | 12 | 12 | 4 | 4 | 5 |
| at Becher St. | 15 | 21 | 18 | 17 | 9 | 8 | 8 |
| at 1st St. | 13 | 18 | 18 | 18 | 16 | 8 | 7 |
| at Kinnickinnic Ave. | 19 | 20 | 20 | 20 | 17 | 12 | 10 |
| | Elevation of water-sediment interface(ft)-IGLD85 | | | | | | |
| Year | 1915 | 1936 | 1944 | 1951 | 1960 | 1978 | 1997 |
| Locations: | | | | | | | |
| at half way between Chase and Linclon Ave., at Lat. 43°00' | 575 | 567 | 567 | 567 | 575 | 575 | 575 |
| at Lincoln Ave. | 568 | 560 | 566 | 566 | 574 | 574 | 573 |
| at Becher St. | 563 | 557 | 560 | 561 | 569 | 570 | 570 |
| at 1st St. | 565 | 560 | 560 | 560 | 562 | 570 | 571 |
| at Kinnickinnic Ave. | 559 | 558 | 558 | 558 | 561 | 565 | 568 |

* Note: apparently since 1960 sounding has not been conducted upstream from Lincoln Ave

** Chart datum was the same until later 1960s. The 1978 chart was created based on the International Greate Lakes Datum (IGLD)1955, while the reference datum changed again on the 1997 chart which was based on IGLD1985.

Table 6. Estimation of sedimentation rates for Cores KK0202 and KK0209 based on the Milwaukee Estuary nautical charts

| Sediment Core 2 | | | | |
|------------------------|---------------------------|---------------------------|------------------|---|
| Chart Year | Elevation (ft) | Diff Elev (ft) | Diff Year | Approx. sedimentation rate (ft/yr) |
| 1936 | 557 | -- | | |
| 1944 | 560 | 3 | 8 | 0.38 |
| 1951 | 561 | 1 | 7 | 0.14 |
| 1960 | 567 | 6 | 9 | 0.67 |
| 1978 | 569 | 3 | 18 | 0.15 |
| 2002 | 574 | 4 | 24 | 0.18 |

| Sediment Core 9 | | | | |
|------------------------|---------------------------|---------------------------|------------------|---|
| Chart Year | Elevation (ft) | Diff Elev (ft) | Diff Year | Approx. sedimentation rate (ft/yr) |
| 1936 | 560 | -- | -- | -- |
| 1944 | 562 | 2 | 8 | 0.25 |
| 1951 | 562 | 0 | 7 | 0.00 |
| 1960 | 563 | 1 | 9 | 0.11 |
| 1978 | 573 | 10 | 18 | 0.56 |
| 2002 | 574 | 1 | 24 | 0.06 |

Table 7. General parameters for samples collected on Feb. 27, 2003

| Sample ID | WD* ft | Elev ft | Time | Color&Texture | Sand % | Silt % | Clay % | Analyses | Notes | Location | |
|-----------|-----------|------------|-------|---|-----------|-----------|-----------|------------|-------|-------------|-------------|
| | | | | | | | | | | Lat | Long |
| KKUS03-01 | 4.0 | 573.5 | 11:30 | Sandy | 98 | 0 | 2 | PAH PCB | | 43° 00' 21" | 87° 54' 50" |
| KKUS03-02 | 2.2 | 575.3 | 11:45 | Sandy | 97 | 1 | 2 | PAH PCB | | 43° 00' 21" | 87° 54' 50" |
| KKUS03-03 | 3.5 | 574.0 | 12:00 | Sandy | 97 | 1 | 2 | PAH | | 43° 00' 15" | 87° 54' 47" |
| KKUS03-04 | 5.2 | 572.3 | 12:15 | Sandy, black asphalt, mussel shells | 95 | 4 | 1 | PAH PCB | | 43° 00' 12" | 87° 54' 44" |
| KKUS03-05 | 9.8 | 567.8 | 12:30 | Silty sand | 93 | 5 | 2 | PAH | | 43° 00' 09" | 87° 54' 42" |
| KKUS03-06 | 3.2 | 574.3 | 12:45 | Sewer smell, gravel, stones, silty sand | 97 | 2 | 1 | PAH PCB | | 43° 00' 05" | 87° 54' 40" |
| KKUS03-07 | 1.8 | 575.7 | 13:00 | gravel, stone, silt sand. | 98 | 0 | 2 | PAH | 1 | 43° 00' 02" | 87° 54' 40" |
| KKUS03-08 | 0 | 577.5 | 13:40 | exposed deposit materials, sandy | 88 | 4 | 8 | PAH PCB | 2 | 42° 59' 52" | 87° 54' 42" |
| KKUS03-09 | 0 | 577.5 | 14:00 | exposed deposit materials, sandy | 98 | 0 | 2 | PAH PCB | 2 | 42° 59' 46" | 87° 54' 48" |

*WD: Water depth

1. No materials could be retained by the ponar. A spoon was used to collect the sample
2. There were no standing water above sand bars. The samples for 08 and 09 were composit samples generated from three subsamples collected with a spoon from two transacts. The middle of the transact was considered as the sample location.

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Fig. 1 Project area and sediment sampling locations



Fig. 2 Businesses currently located in the project area (SEWRPC, 2000)



Fig. 3 Number of boats registered in Wisconsin (WDNR, 2003)

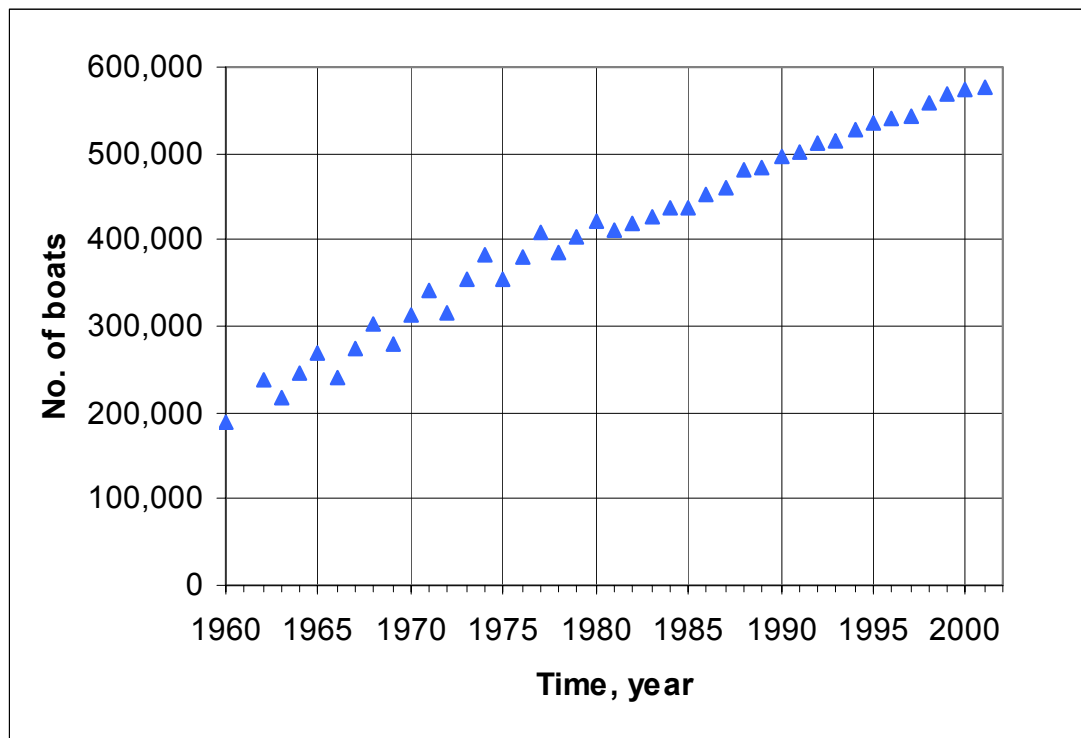


Fig. 4 Locations of businesses during 1930s and 1950s (Sanborn maps)

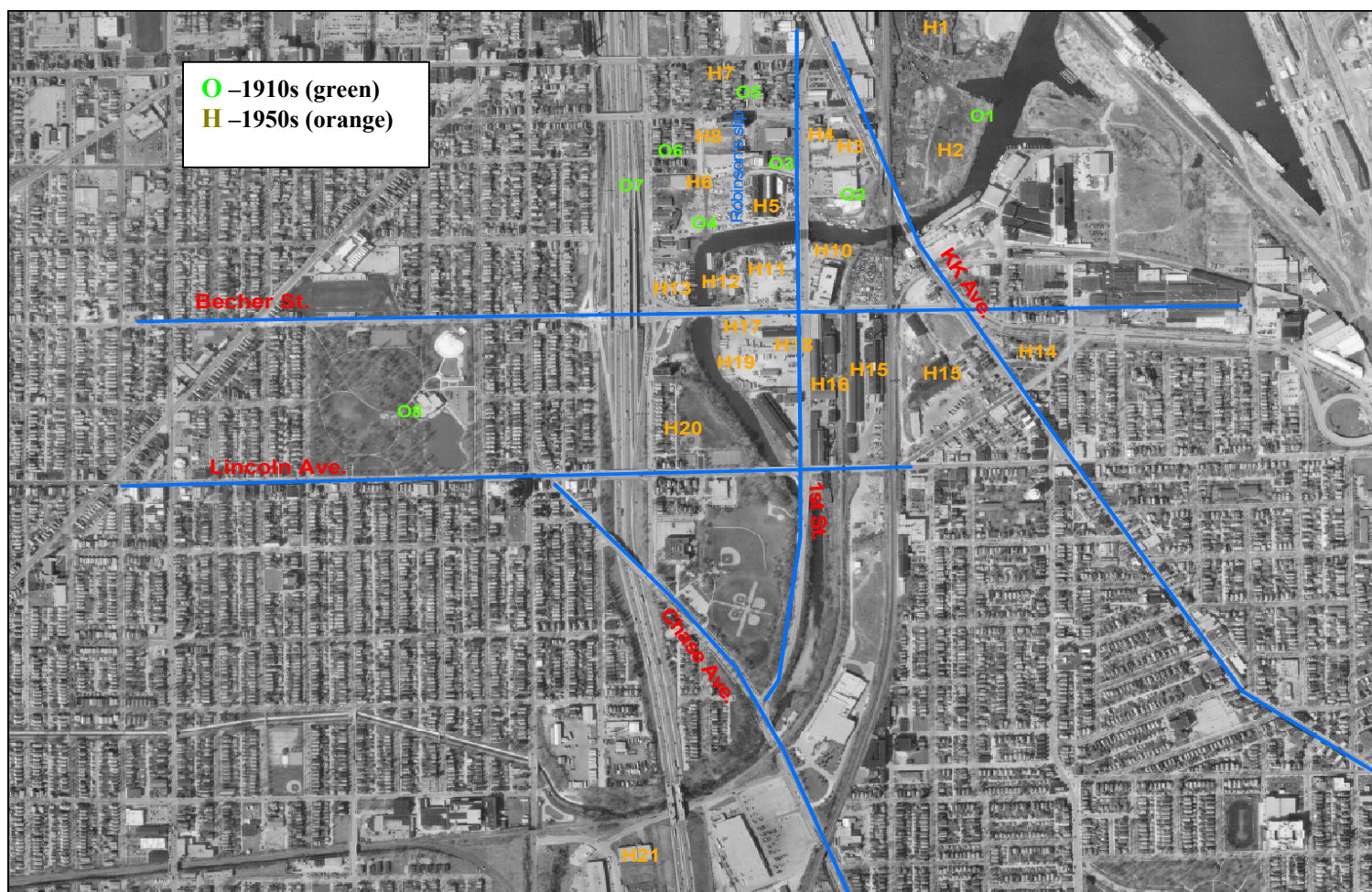


Fig. 5 Sounding data (1915)

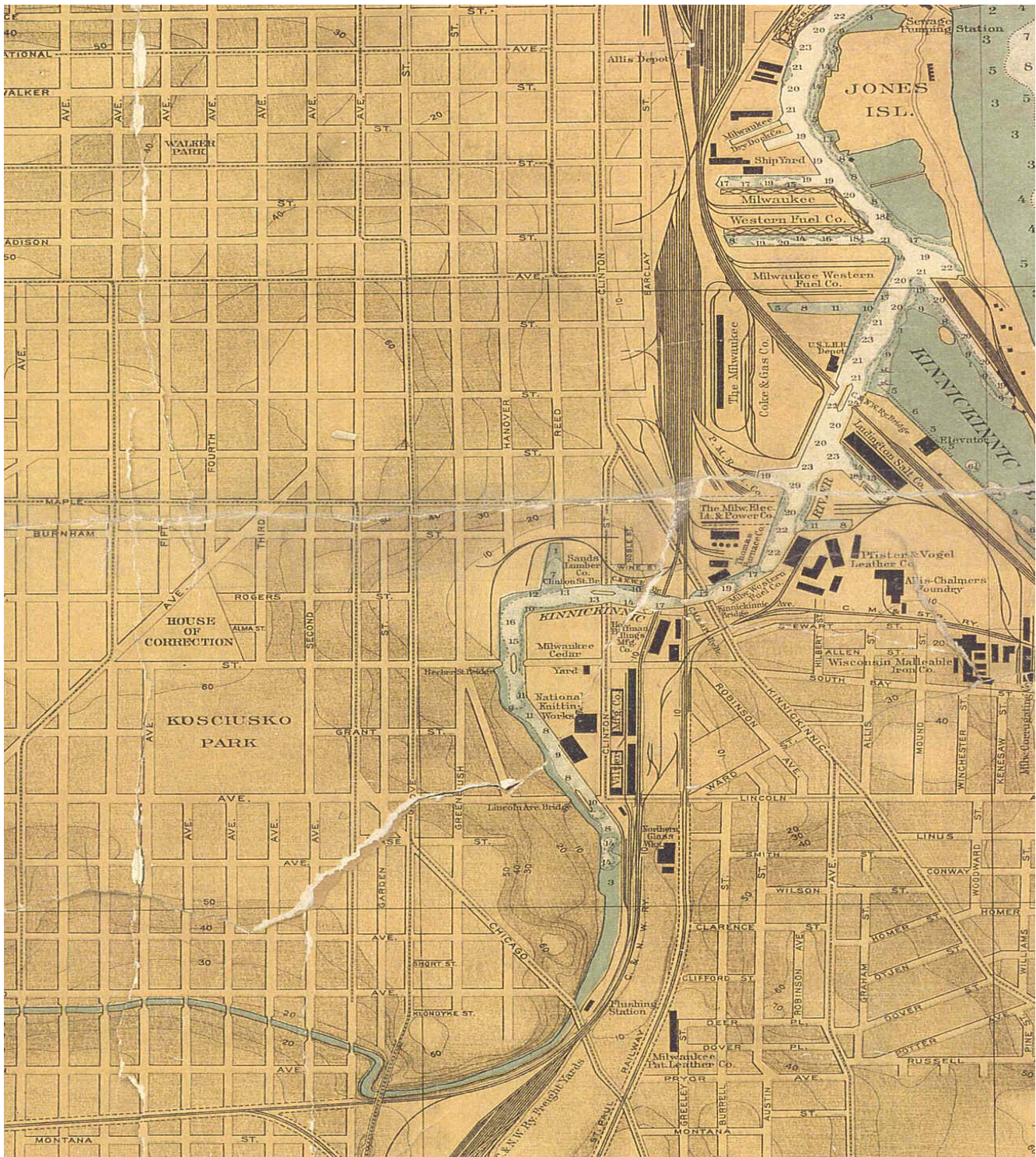


Fig. 6 Sounding data (1936)

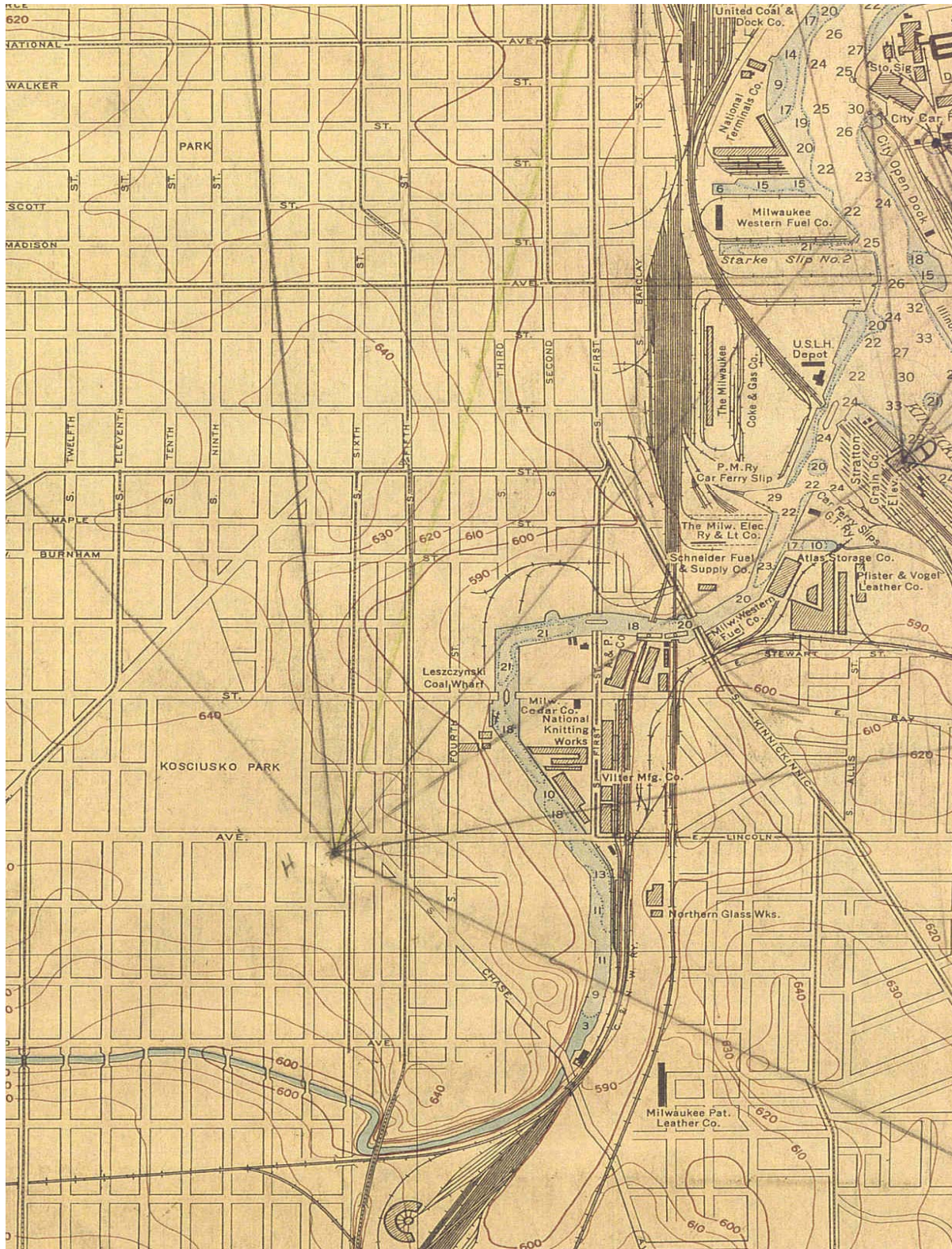


Fig. 7 Sounding data (1944)

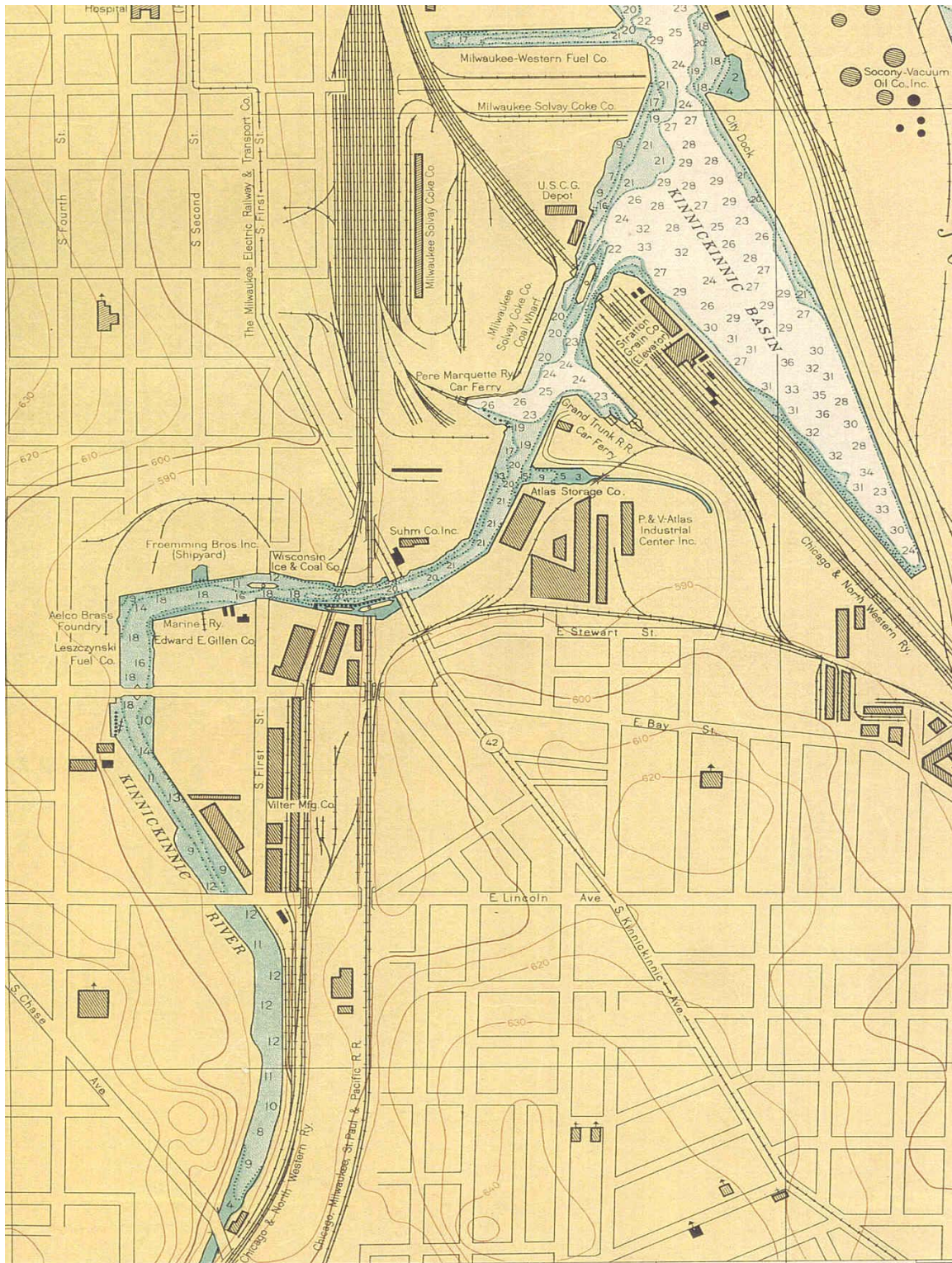


Fig. 8 Sounding data (1951)

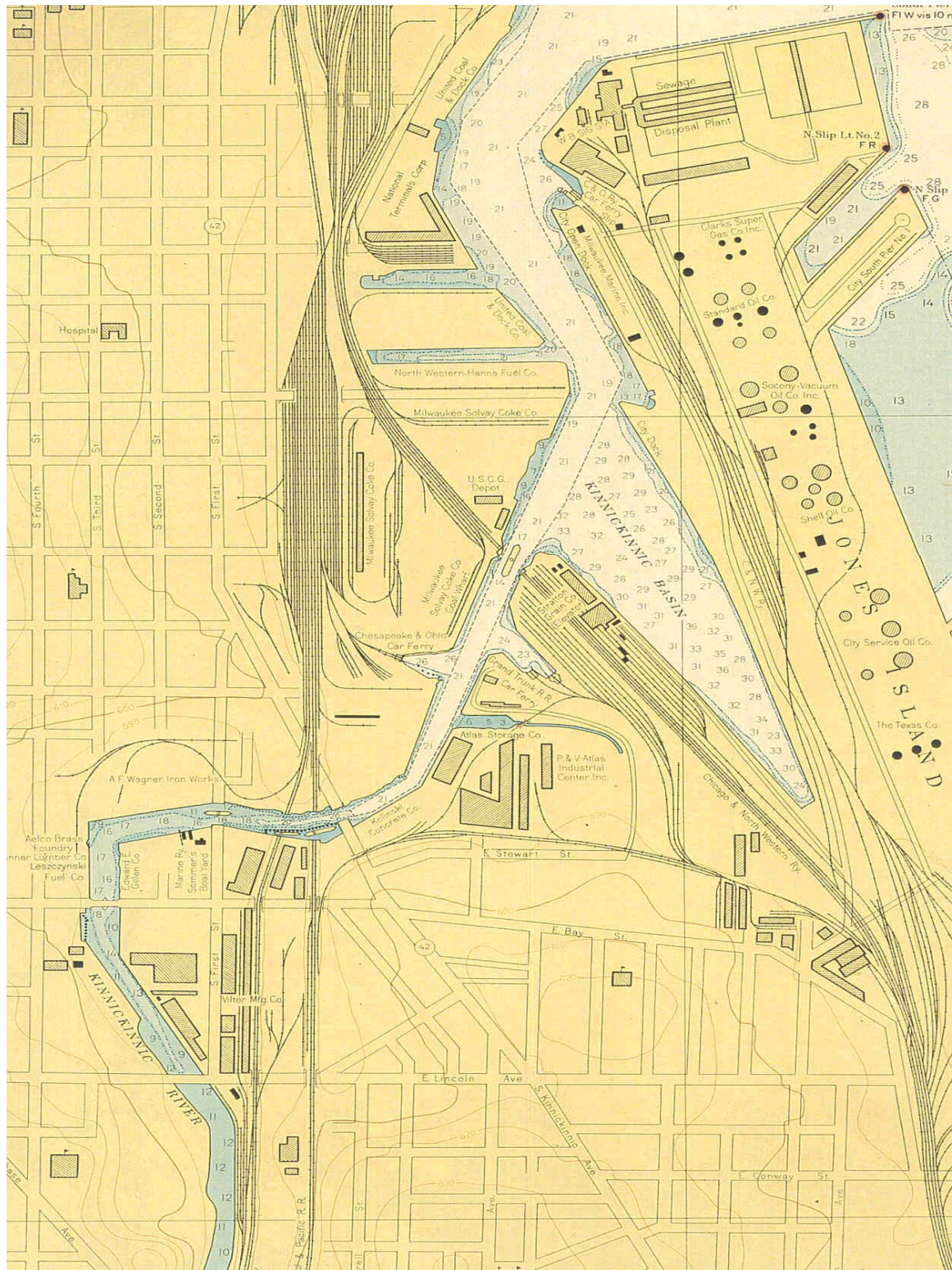


Fig. 9 Sounding data (1960)



Fig. 10 Sounding data (1978)



Fig. 11 Sounding data (1997)



Fig. 12 Profiles of PCBs and PAHs in sediment cores KK0202 and KK0209 with estimated sedimentation dates based on the historical nautical charts

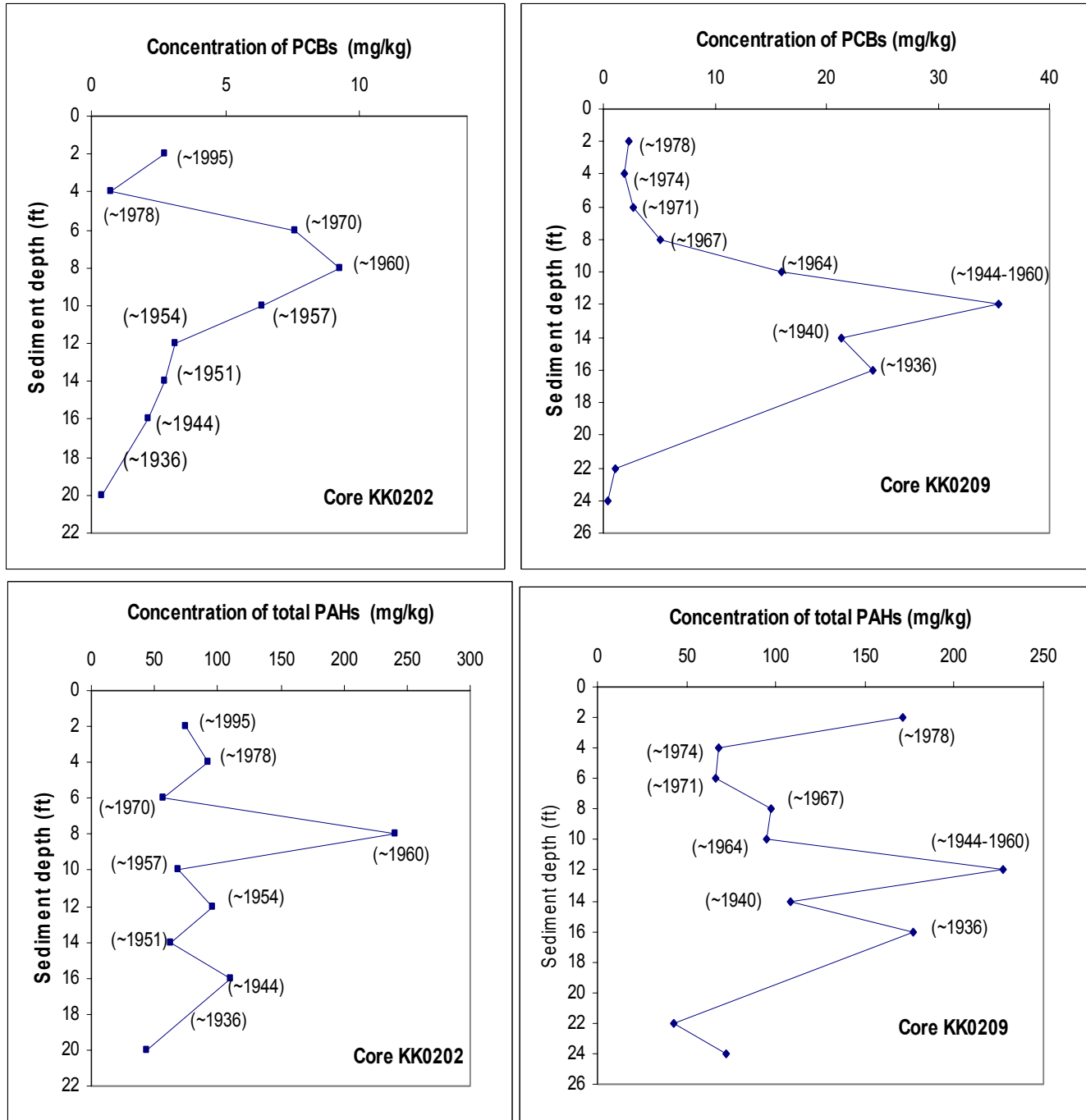


Fig. 13 Comparison of PCB and PAHs in background sediment with that in the surface sediment from the project area

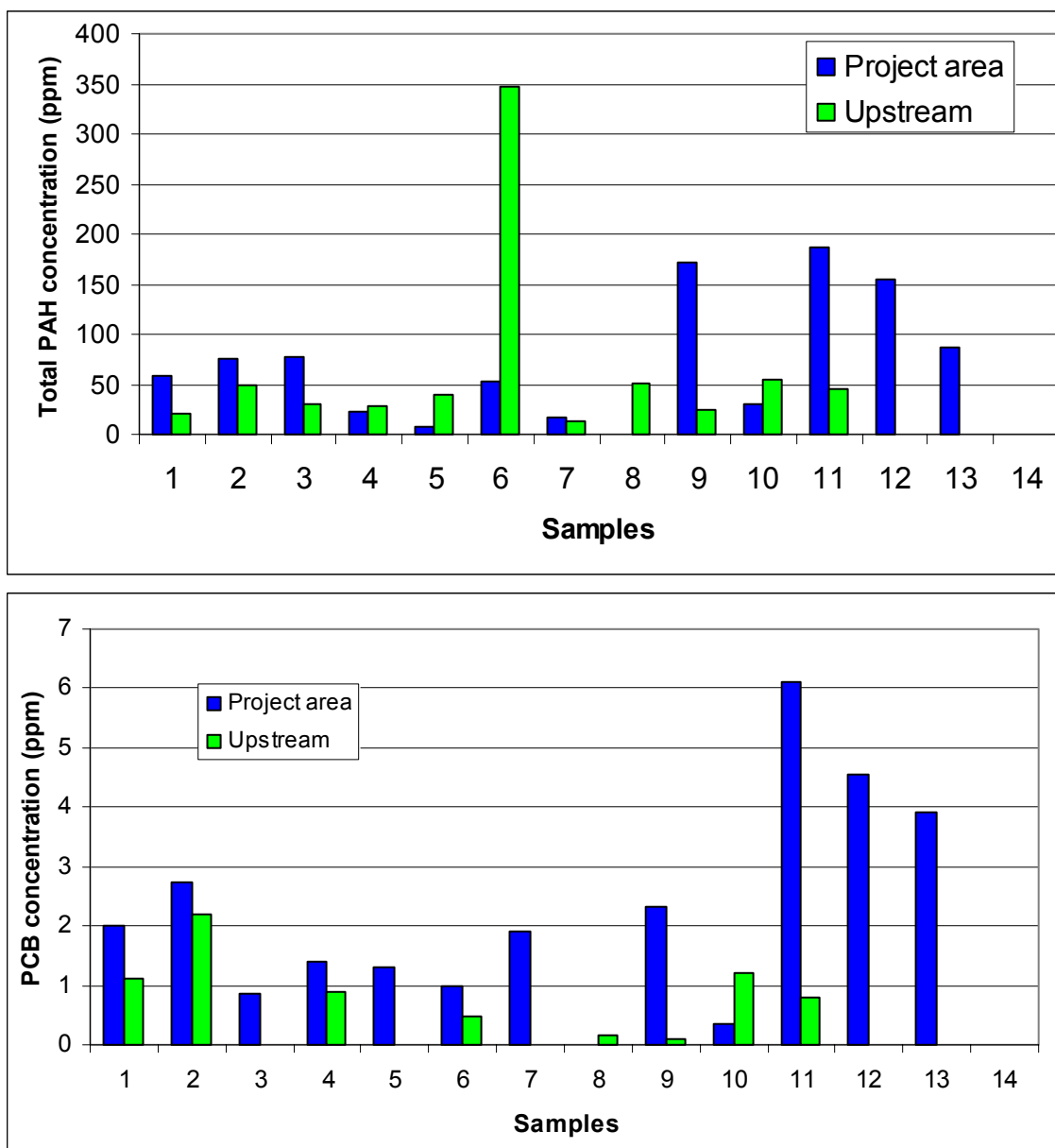


Fig. 14 PCB assemblage in sediment from the KK River between Chase Ave. and Kinnikinnic Ave.

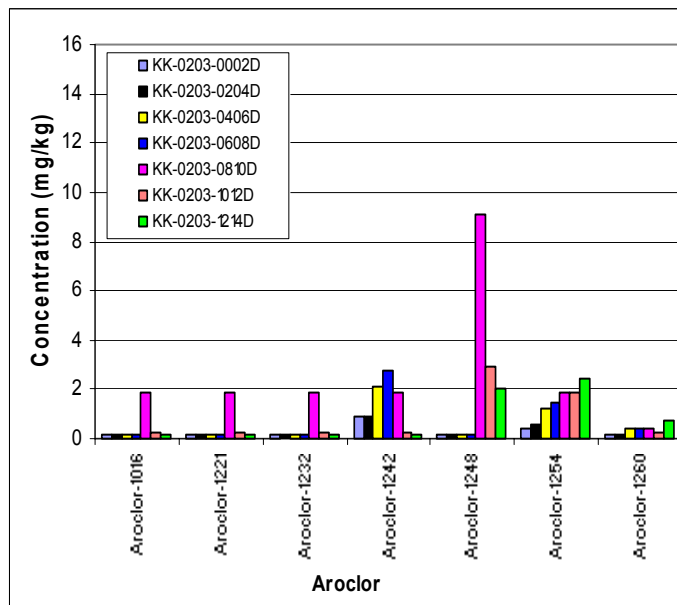
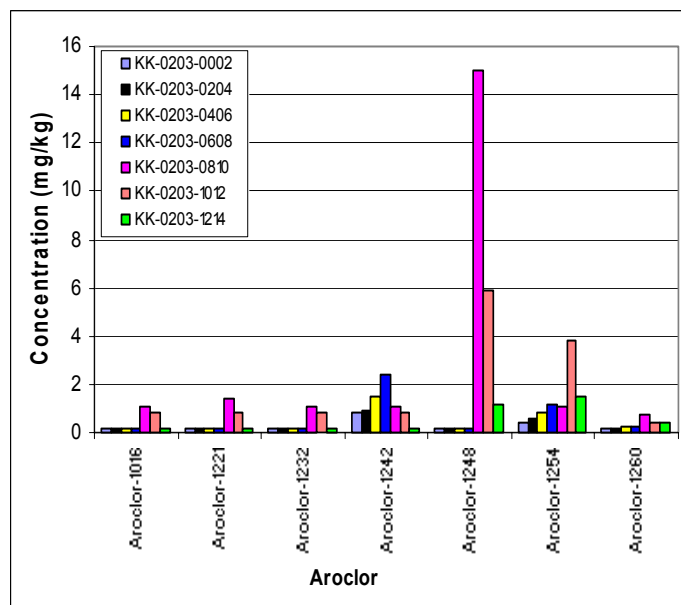
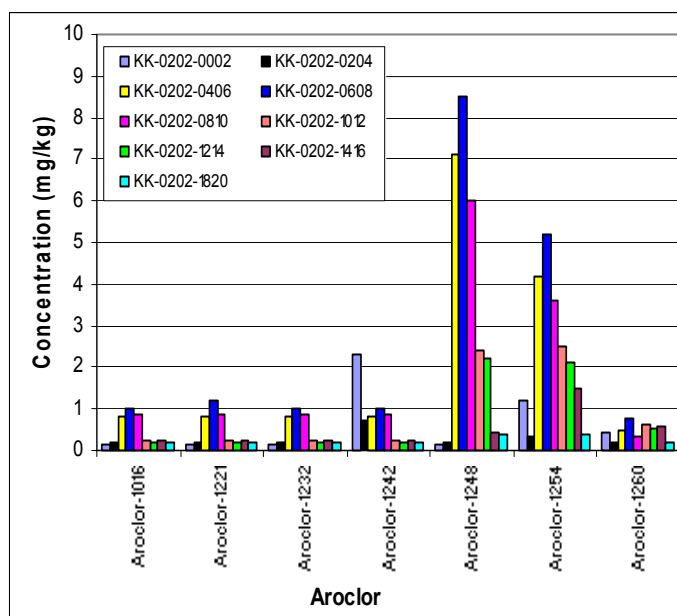
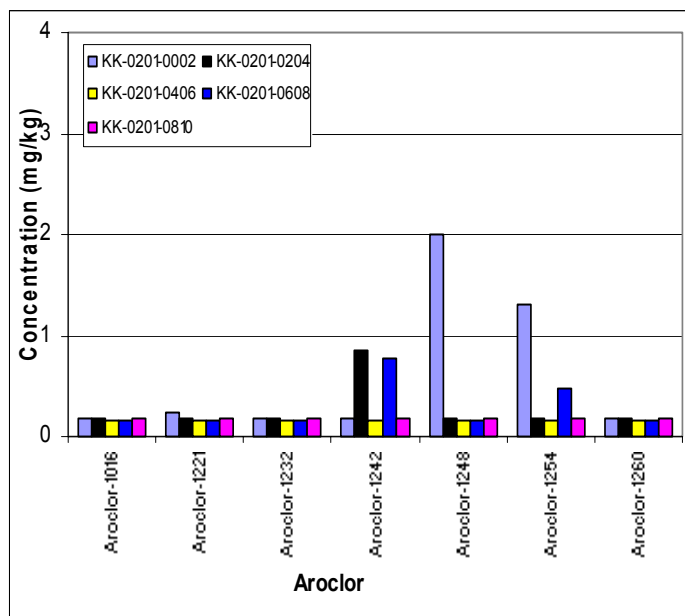


Fig. 14 (Cont'd)

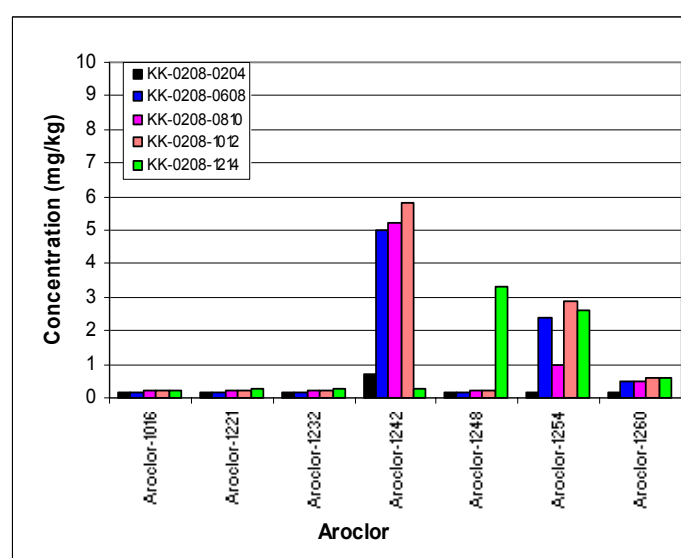
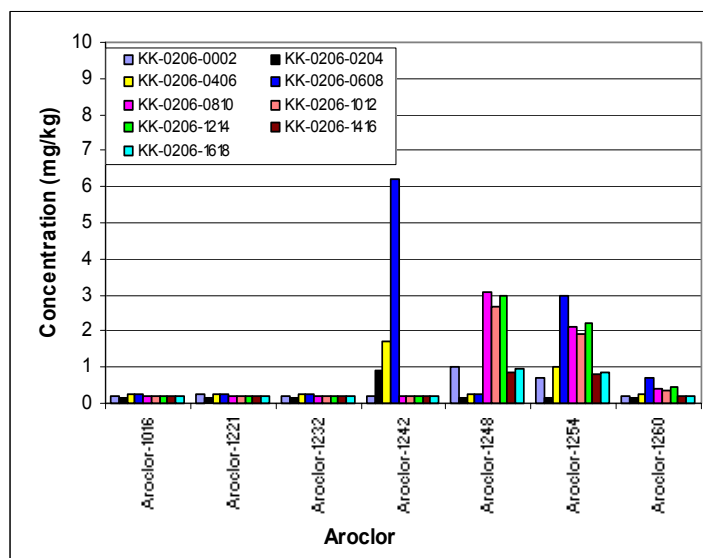
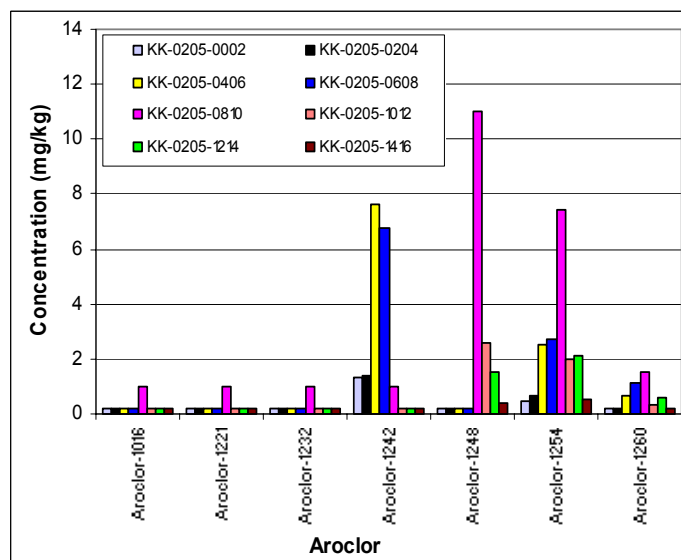
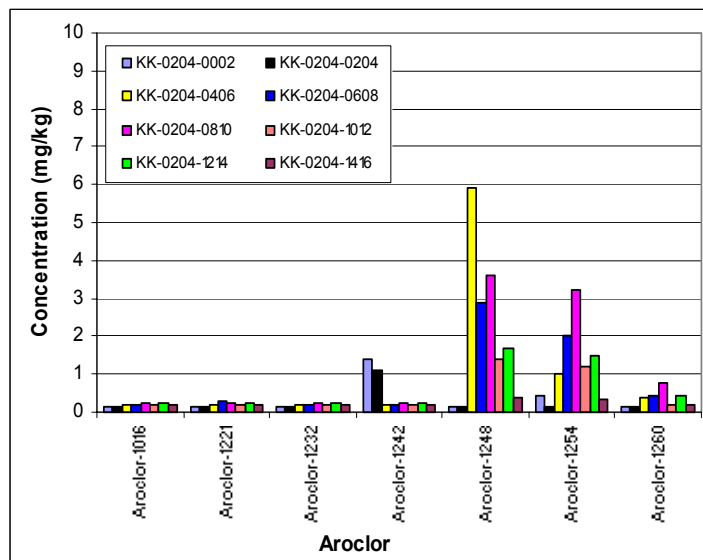


Fig. 14 (Cont'd)

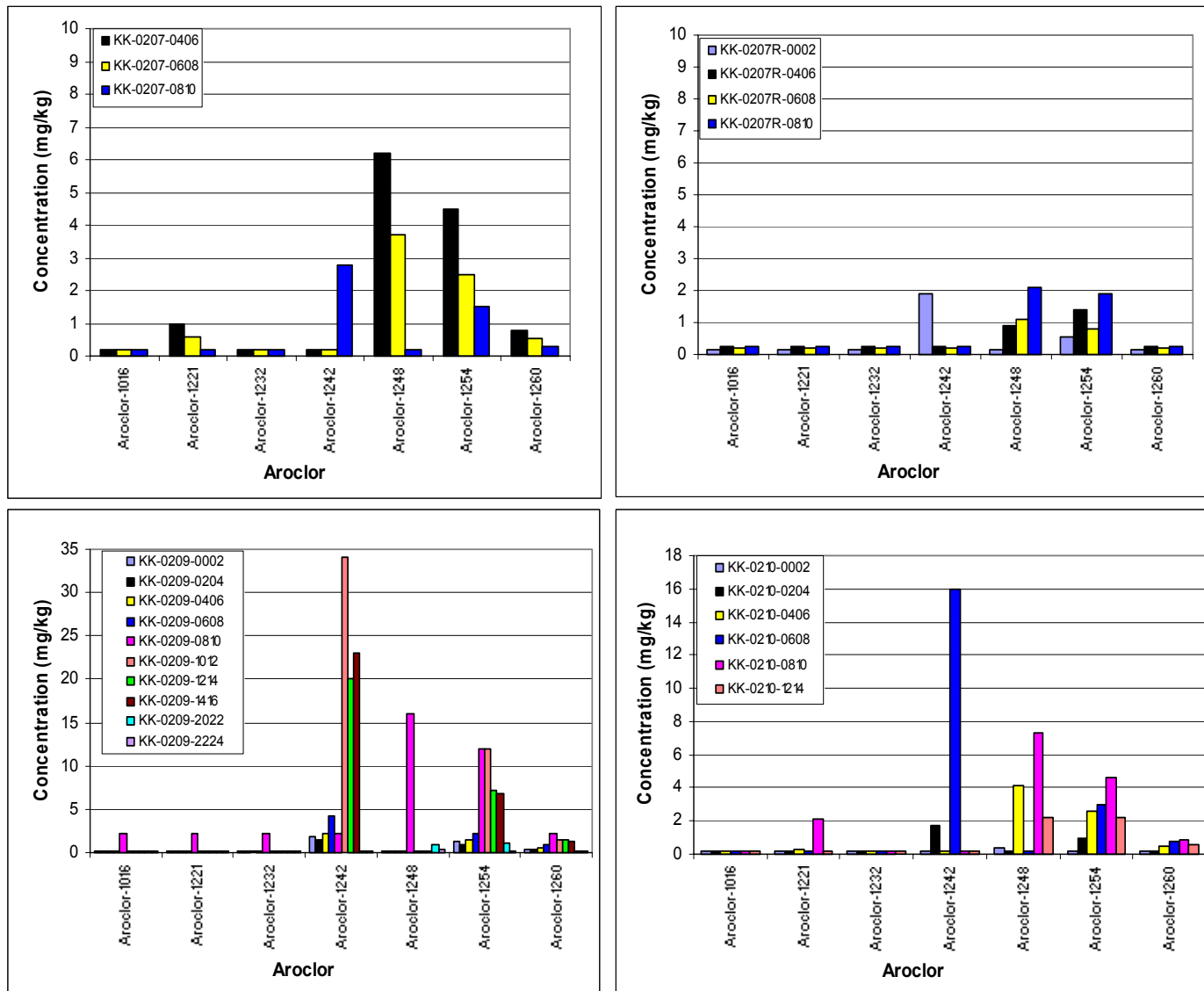


Fig. 14 (cont'd)

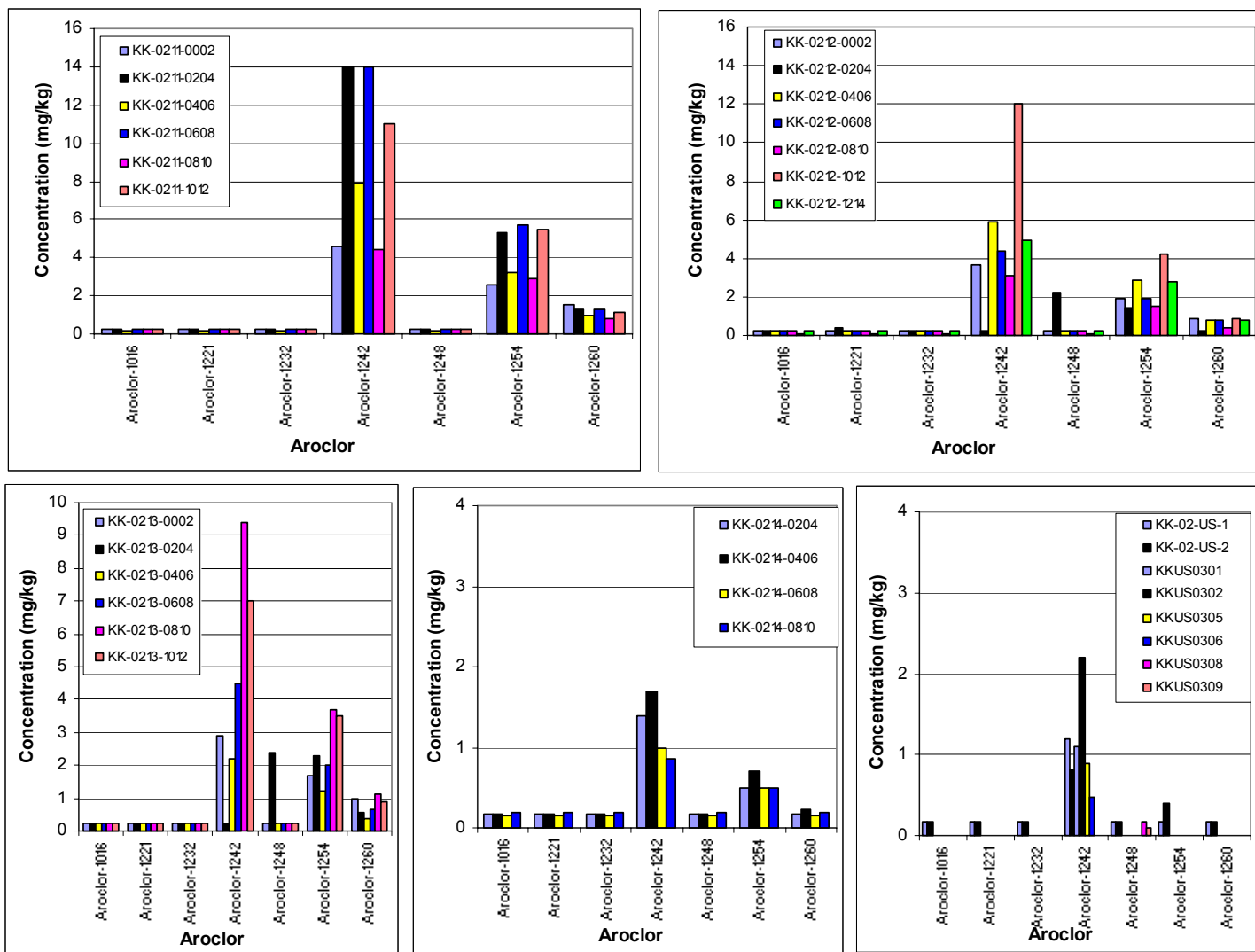


Fig. 15 C16 normalized PAHs in tar, heavy oil, soil, and pit materials collected from SC MGP site (Tetra Tech, 2002)

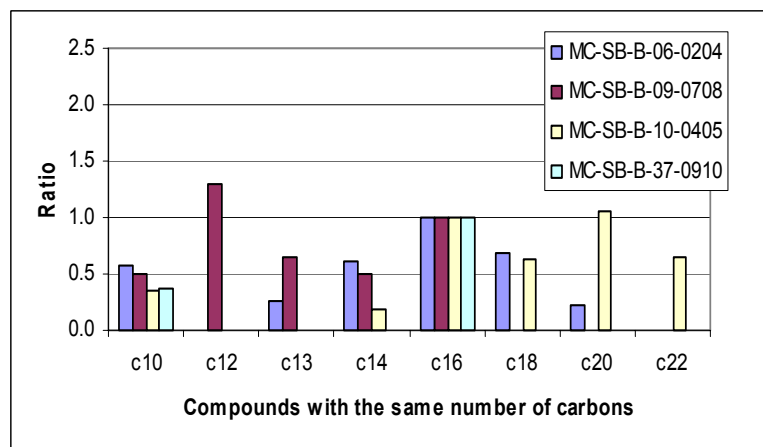
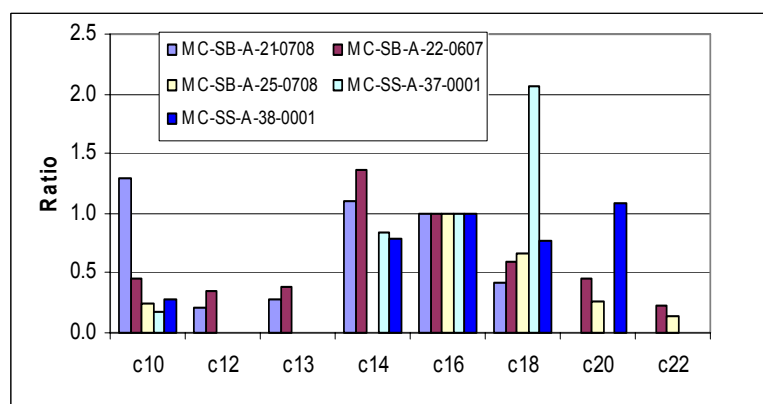
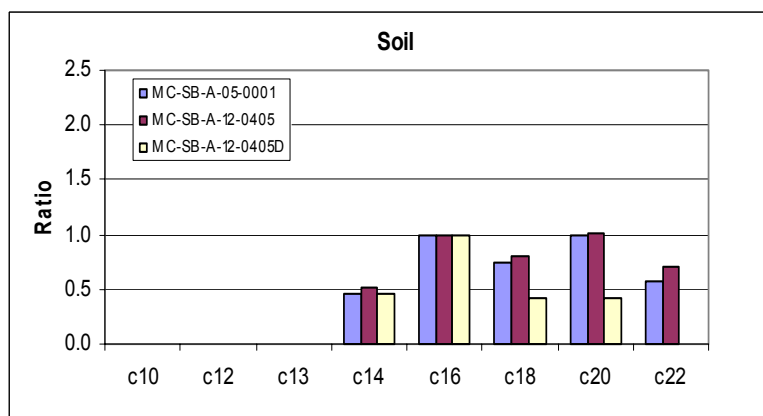
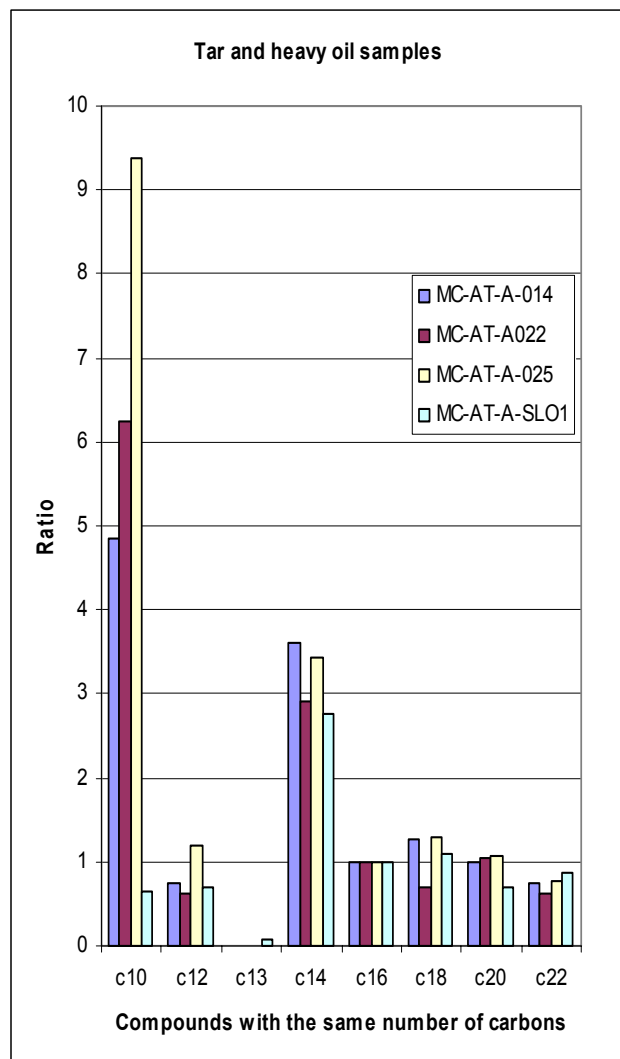


Fig. 16 C16 normalized PAHs in sediment collected from the MSCG site (Tetra Tech 2002)

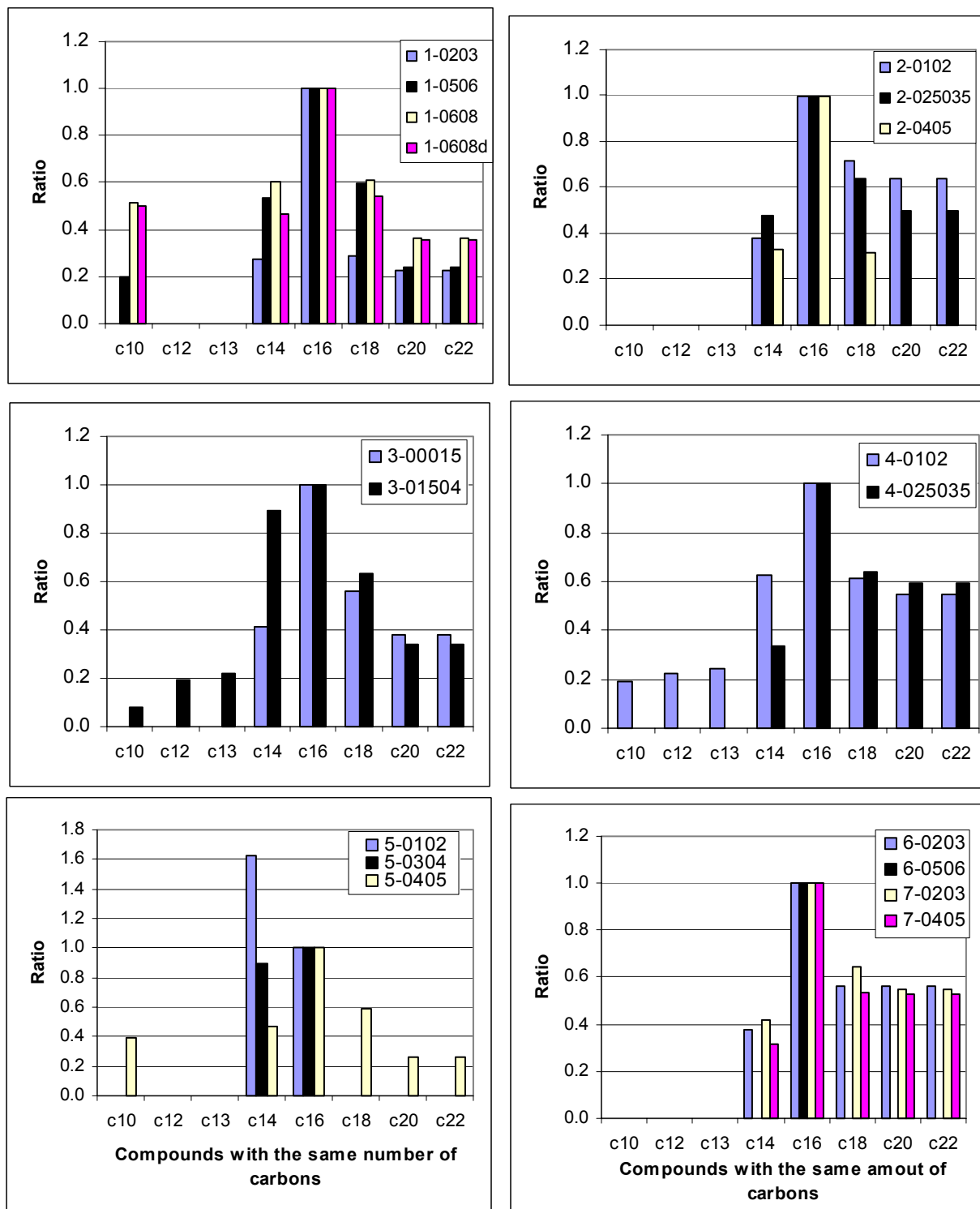
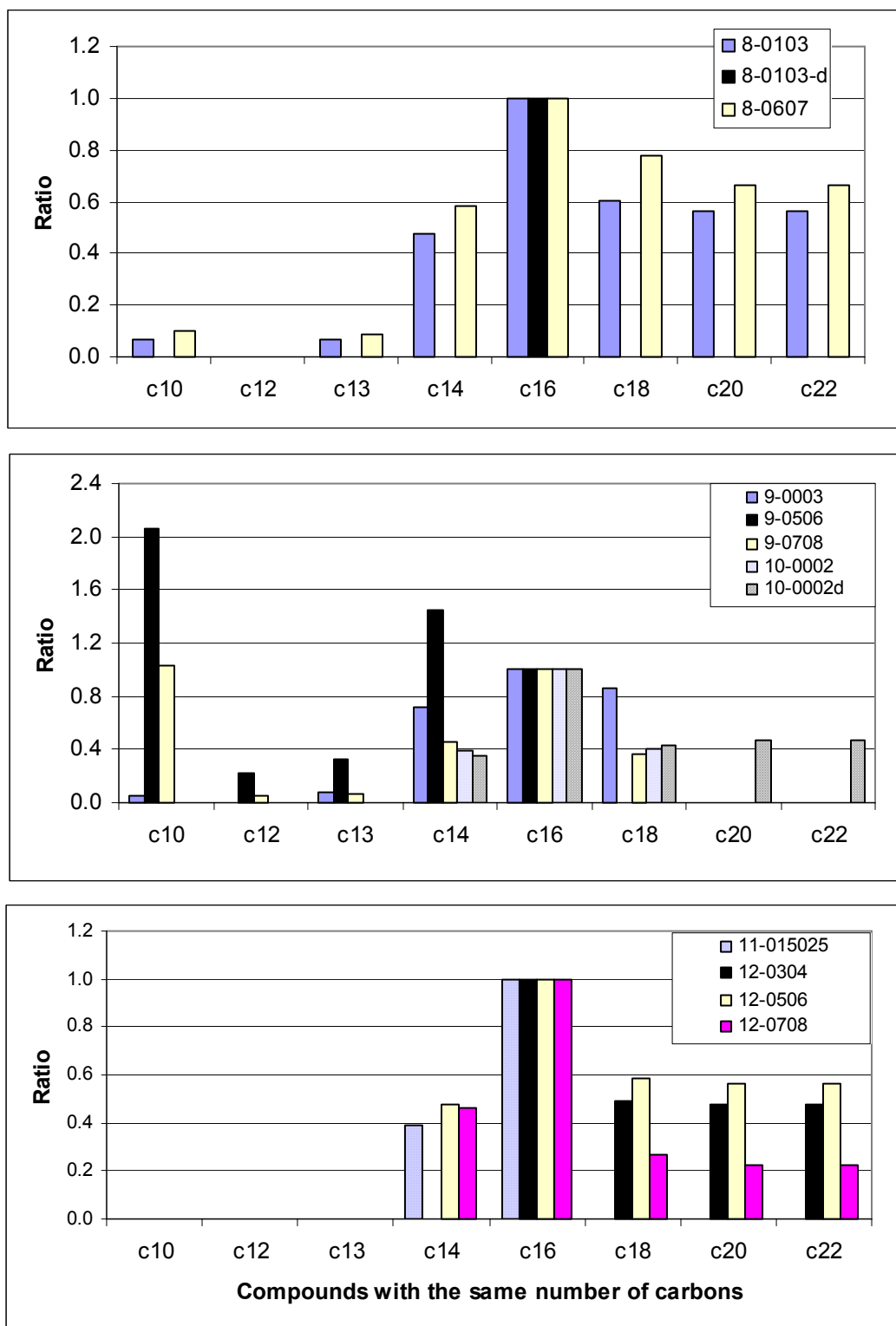


Fig. 16 (cont'd)



**Fig. 17 C16 normalized PAHs in sediment from the KK River
(Altech 2002)**

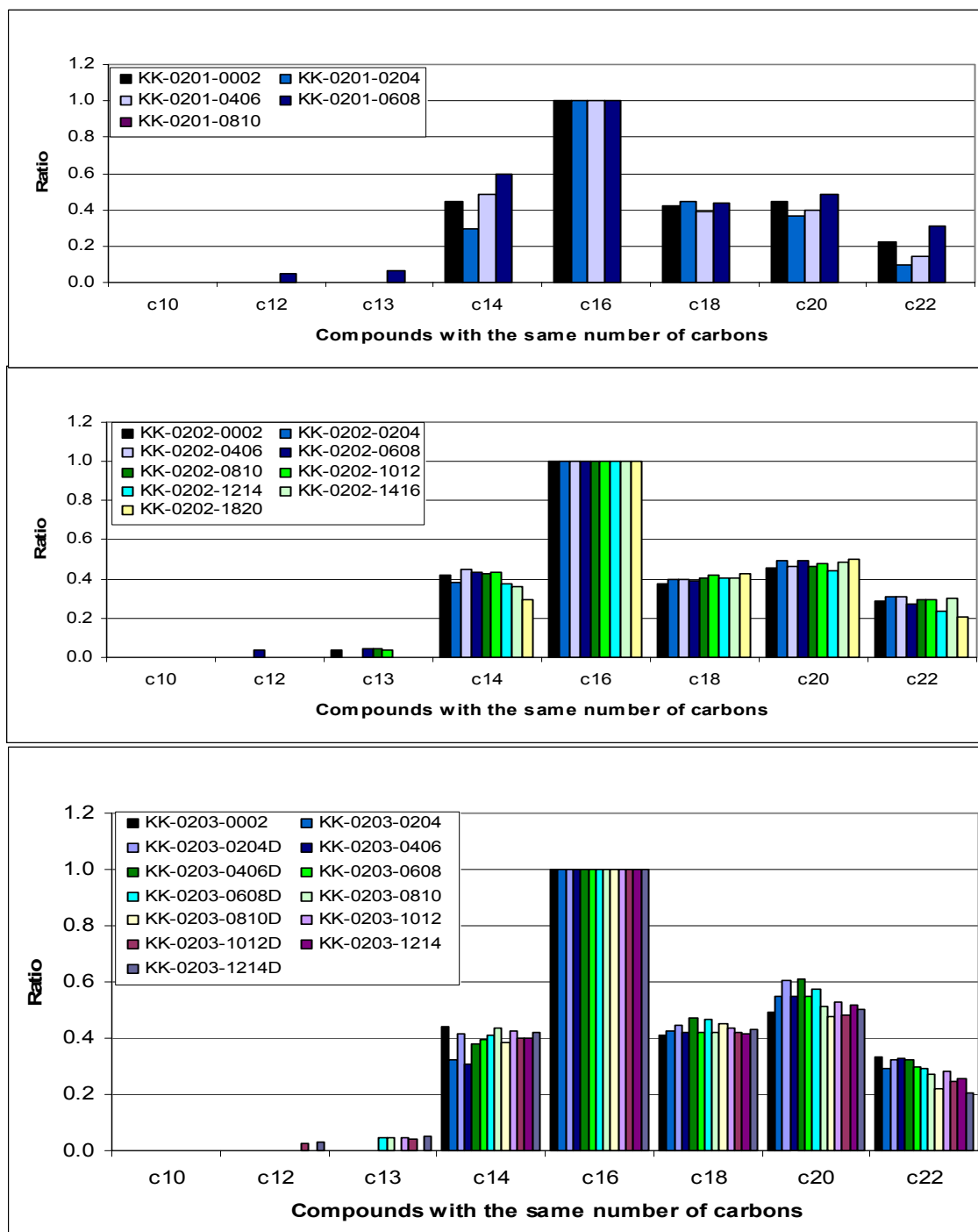


Fig. 17 (cont'd)

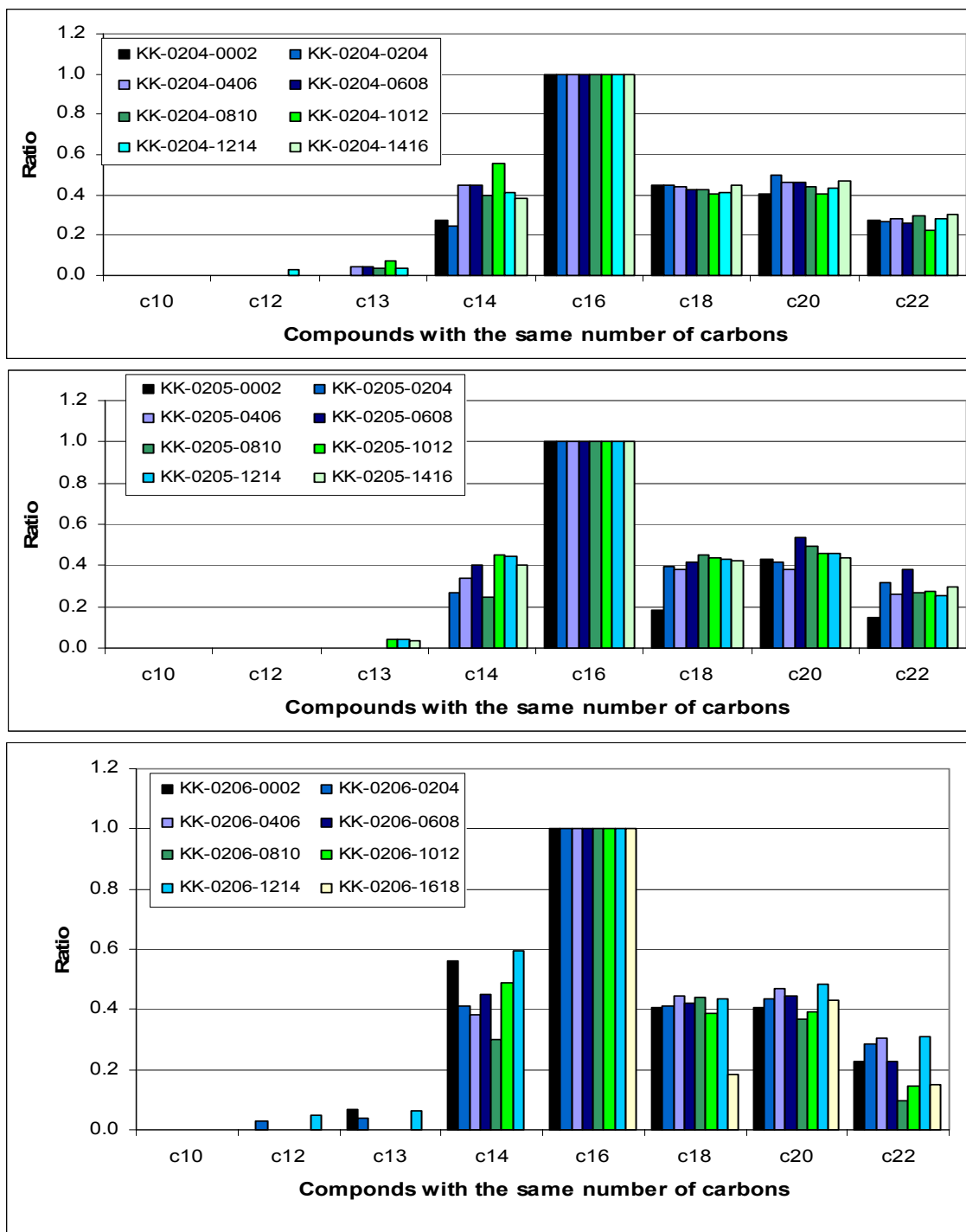


Fig. 17 (cont'd)

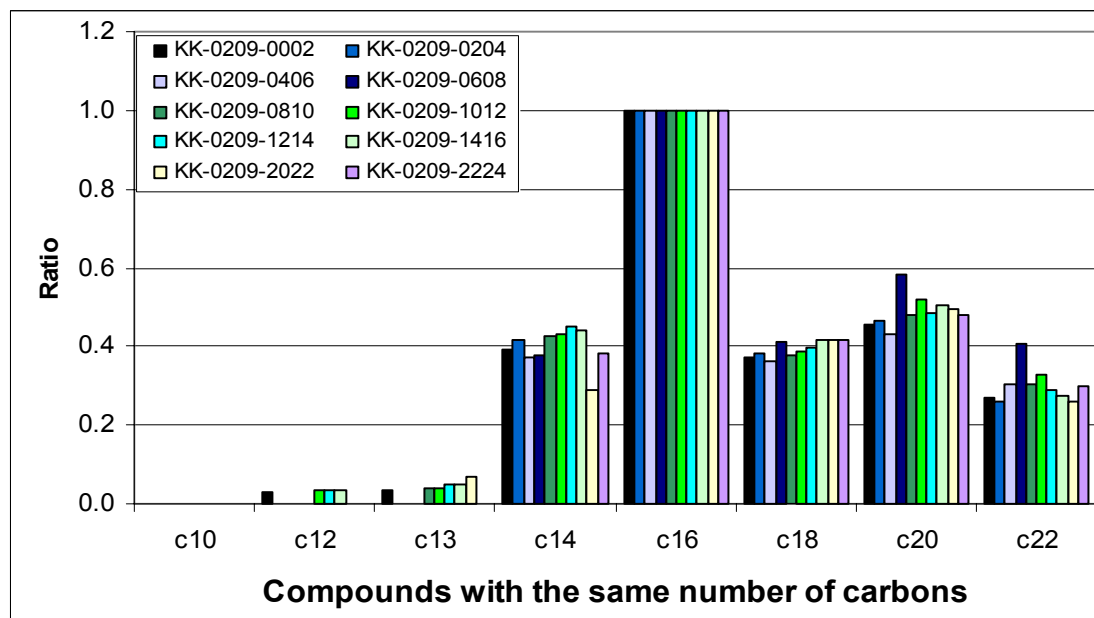
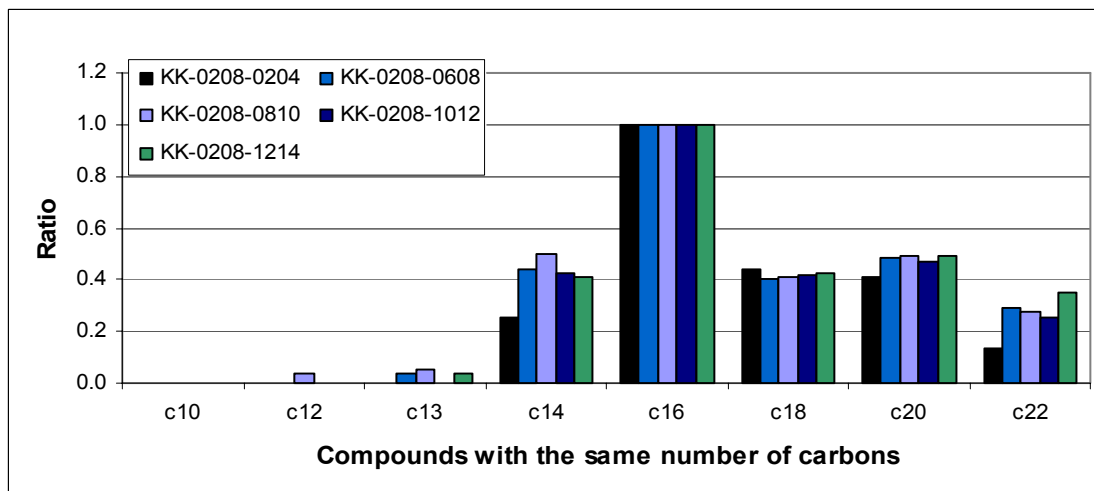
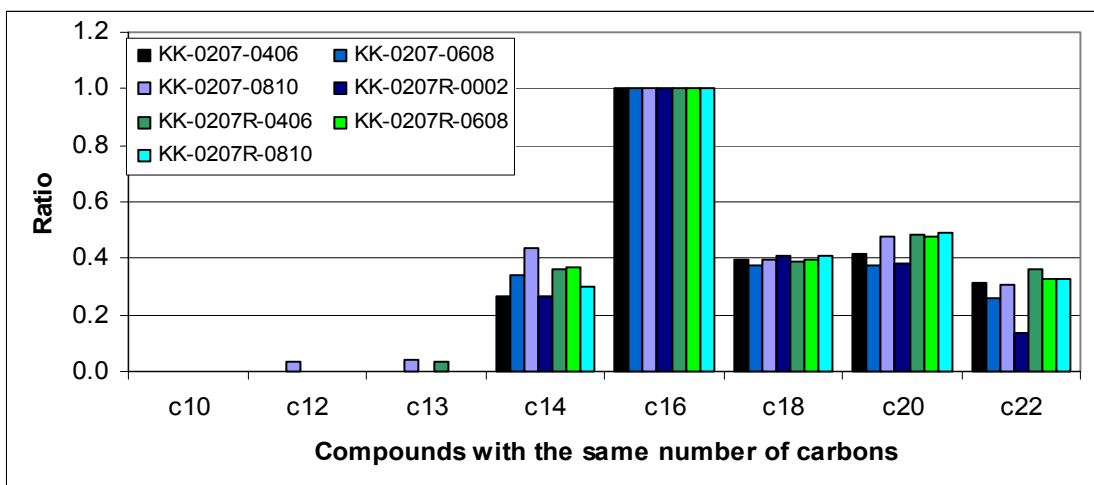


Fig. 17 (cont'd)

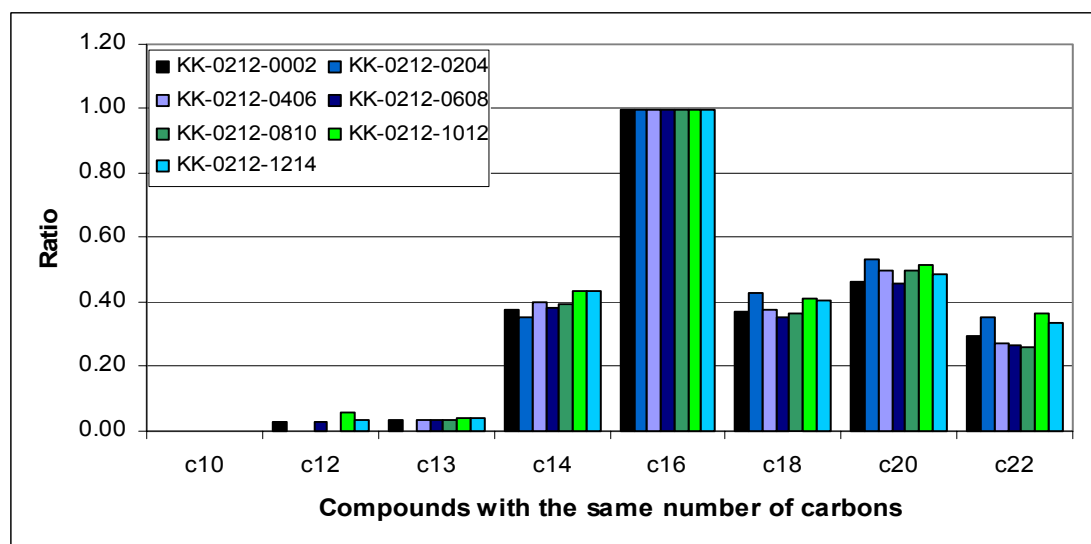
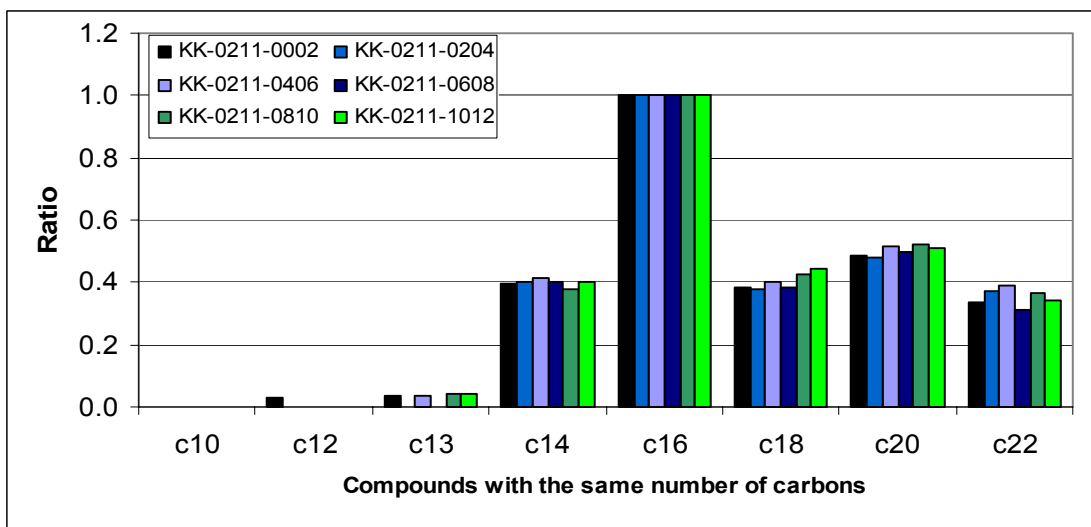
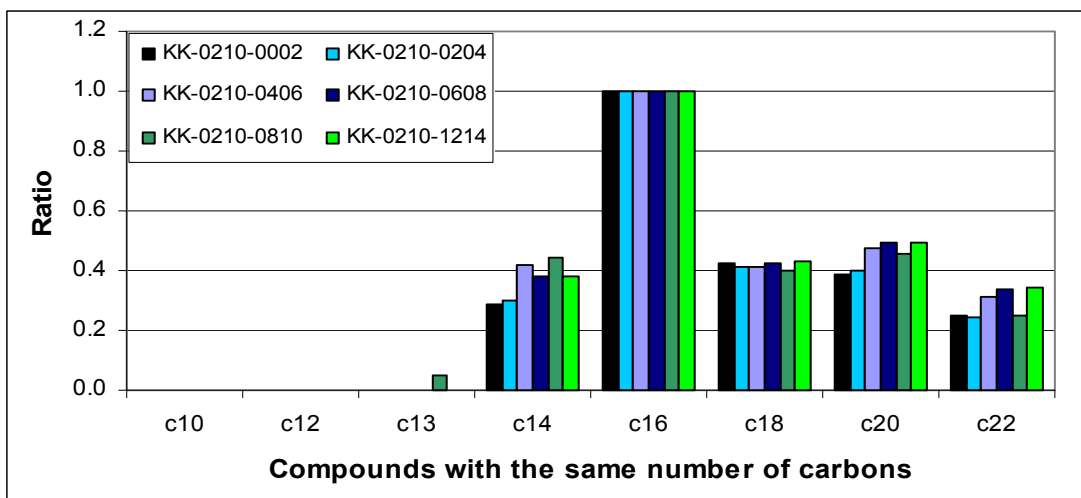


Fig. 17 (cont'd)

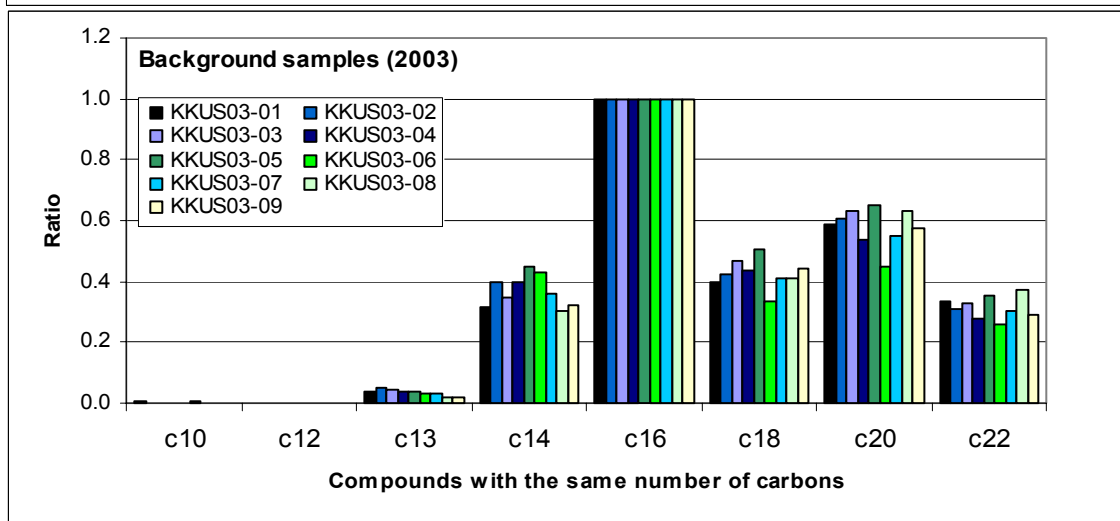
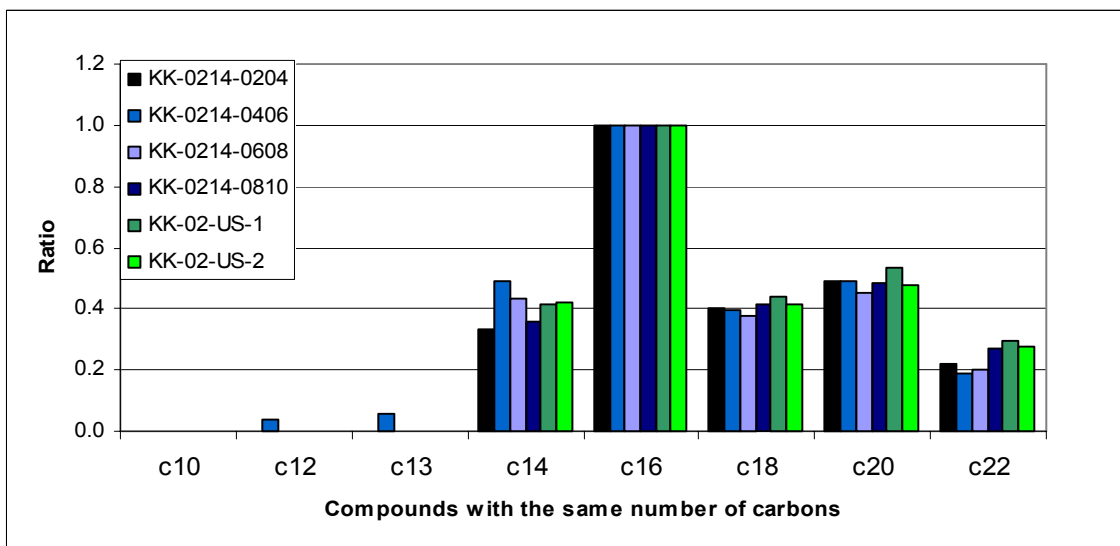
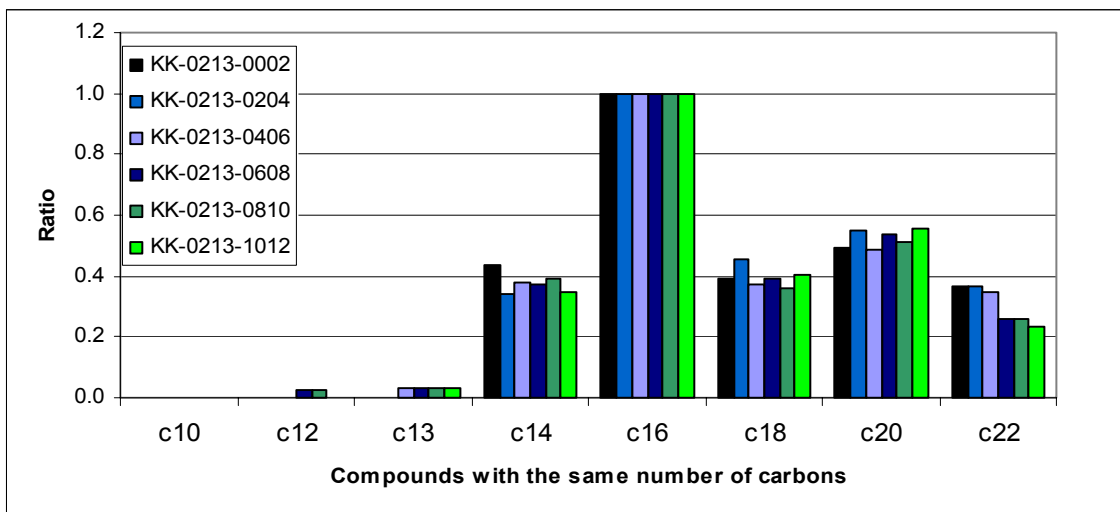


Fig. 18 C16 normalized PAHs in nonpoint sources

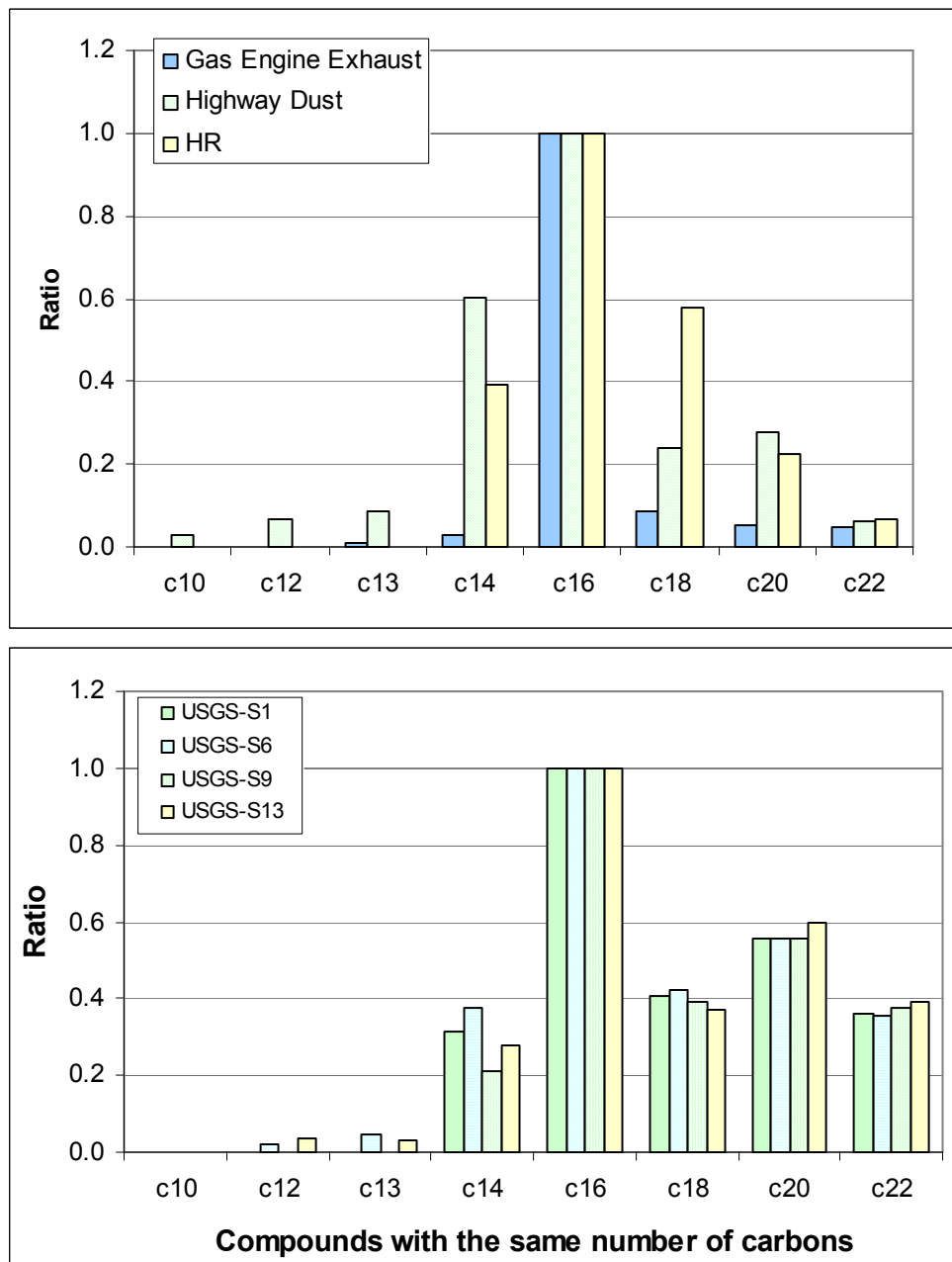


Fig. 19 Distribution of parent and c-substituted PAHs in selected sediment samples (Altech 2002)

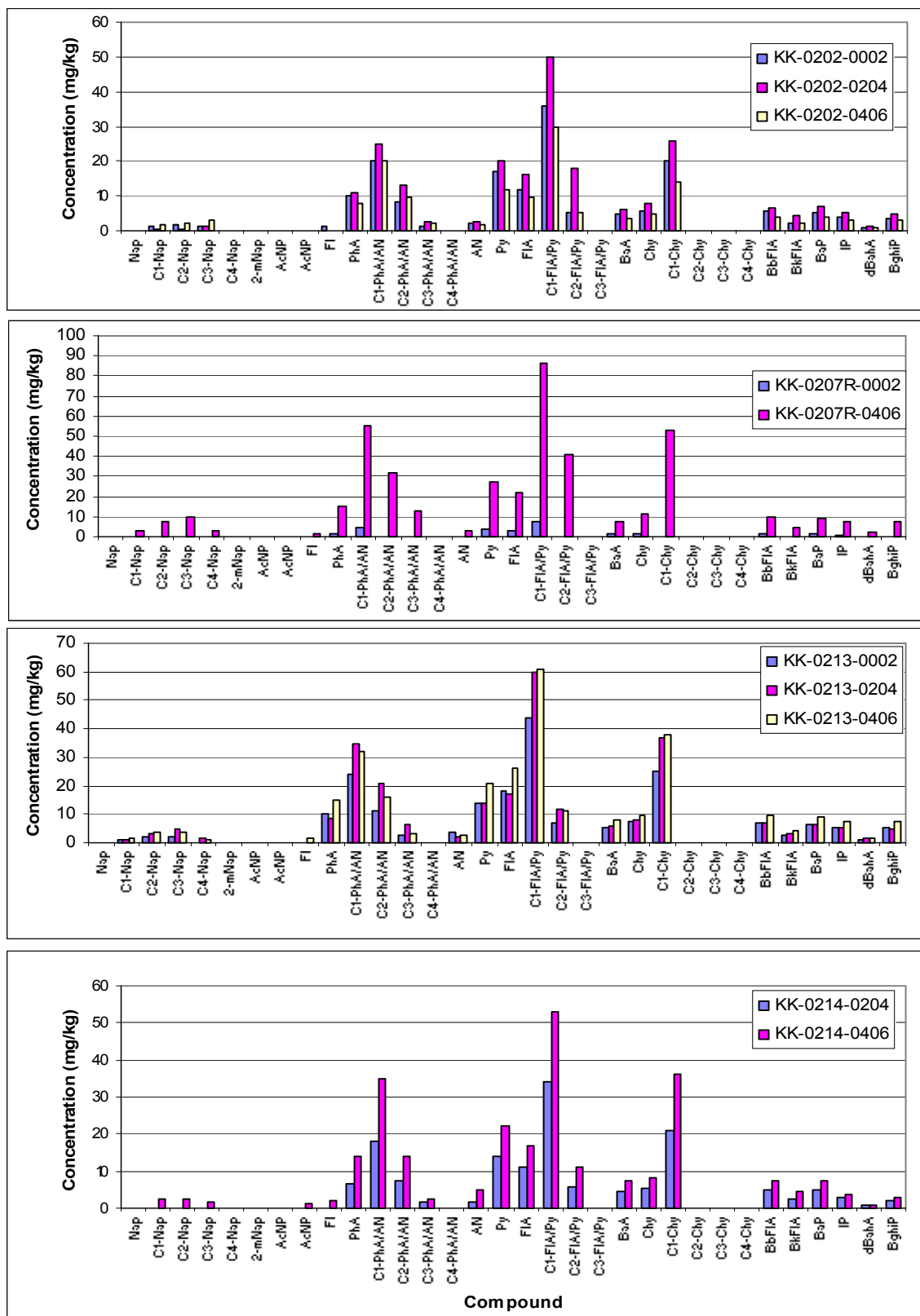


Fig. 19 (cont'd)

